





Preparation, Characterization and CO Oxidation Performance of Ag_2O/γ - Al_2O_3 and $(Ag_2O+RuO_2)/\gamma$ - Al_2O_3 Catalysts

Antony Ananth[®], Rak Hyun Jeong and Jin-Hyo Boo *

Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea; dr.ananth@skku.edu (A.A.); jrh1015@naver.com (R.H.J.)

* Correspondence: jhboo@skku.edu; Tel.: +82-31-290-7072; Fax: +82-31-290-7075

Received: 29 May 2020; Accepted: 15 June 2020; Published: 23 June 2020



Abstract: This research dealt with the preparation and characterization of silver oxide (SLO) nanomaterials (NMs) and their composite catalysts (i.e., silver and ruthenium oxide (SLORUO)). The prepared materials were tested for their catalytic performance in carbon monoxide (CO) oxidation. Generally, silver in its pure state is not widely used for CO oxidation due to stability and structural issues. However, the usage of subsurface oxygen and oxygen-induced reconstruction could be effective as an oxidation catalyst at a slightly high temperature. The low-temperature reaction of highly active RuO₂ (RUO) is a well-known phenomenon. Thus, the possibility of using it with SLO to observe the combined catalytic behavior was investigated. The wet chemically prepared SLO and SLORUO NMs exhibited spherical and rods in spherical aggregate-type surface morphology belonging to cubic and rutile crystalline structures, respectively. The NMs and catalysts (i.e., the NMs on γ -Al₂O₃ catalyst support at 0.5 and 1.0 wt.% ranges) showed good thermal stability. The dry and wet CO oxidation using RUO and SLO showed concentration-dependent catalytic activity. The RUO, SLO, and SLORUO composites using 0.5 wt.% showed full CO oxidation at 200, 300, and 225 °C, respectively. The reasons for the observed activity of the catalysts are explained based on the pore characteristics, chemical composition, and dispersion using H₂ temperature-programmed reduction (TPR) behaviors.

Keywords: silver oxide; CO oxidation; ruthenium oxide; Ag₂O/RuO₂; composite

1. Introduction

Air pollution is a serious global issue due to the rapid emergence of industrial, vehicular, and infrastructural proliferation. Gas products emerging out of various sources require proper conversion treatment before being released into the environment. A common toxic gas found in many or even in simple emitters is carbon monoxide (CO). The main source of CO is incomplete fuel combustion. Continuous exposure to 1000 ppm of CO for 1 h will cause respiratory failure, unconsciousness, and even death to humans. Simple thermal catalysis processing using a small number of efficient catalysts made from transition metal oxides, such as ruthenium oxide (RUO) and silver oxide (SLO), can be considered for treating CO.

SLO and RUO are used in many industrial and biomedical applications such as in catalysis, preparation of antimicrobial substances [1,2], energy storage devices [3,4], and electronics [5]. For example, RUO exhibits excellent CO oxidation activity at a lower temperature, where the CO adsorbs on the edge and surfaces in the Ru-O crystal and forms CO₂, which is highly size and shape-selective [6,7]. RuO₂ is slightly expensive, whereas silver is abundant. The lattice oxygen found in the Ag-O structure is responsible for the activity of silver oxide [8], and its performance depends

on the catalyst loading and method of preparation. Many reports show that mixed catalysts, such as $CuMn_2O_4$ and $Cu_2Ag_2O_3$, have rendered an excellent CO oxidation performance. The active oxygen species found on these catalysts act as oxygen suppliers, and the mixed catalysts have demonstrated enhanced redox properties [9]. It has been shown that when silver is used with other active catalysts or supports, it can exhibit excellent stability during operation. This is because of the possibility of Ag_2O to be consumed by CO [10]. Meanwhile, an additional catalyst such as RuO_2 on a stable gamma-alumina (γ -Al₂O₃) support can be utilized. At the same time, reports on the CO oxidation by Ag_2O and its composites (especially with RuO_2) are scarce or not found in the literature. In this background, this research deals with the preparation, characterization of Ag_2O and Ag_2O/RuO_2 NMs, and its catalytic activity in CO oxidation.

2. Materials and Methods

 γ -Al₂O₃ (MW. 101.96 g·mol⁻¹) and polyethylene glycol (PEG, average MW. 20,000 g·mol⁻¹) were procured from Sigma Aldrich Chemie, Gmbh, Berlin, Germany. Moreover, silver nitrate (AgNO₃, MW. 169.87 g·mol⁻¹), ruthenium chloride hydrate (RuCl₃·H₂O, MW. 207.43 g·mol⁻¹), and sodium hydroxide (NaOH, MW. 40 g·mol⁻¹) were also supplied by Sigma Aldrich Chemie, Gmbh, Berlin, Germany.

2.1. Preparation of Ag_2O/γ - Al_2O_3 and $(Ag_2O+RuO_2)/\gamma$ - Al_2O_3 Catalysts

The AgNO₃ (0.01 M), RuCl₃ (0.01 M), NaOH (0.1 M), and PEG (0.2 mM) solutions were prepared separately using deionized water, and 25 mL of each solution was used for the experiment. To prepare Ag₂O NMs, the AgNO₃, NaOH, and PEG solutions (acting as a template and not involved in chemical reaction) were reacted at 75 °C for 6 h in a burette and beaker setup at 500 rotations per minute. The chemical reaction equation for the formation of silver oxide is given in Equation (1).

$$AgNO_3 + NaOH \rightarrow Ag(OH) + NaNO_3$$
(1)

$$RuCl_3 + 3NaOH \rightarrow Ru(OH)_3 + 3NaCl$$
 (2)

At the end of the reaction, dark brown silver hydroxide was formed and rinsed several times with deionized water. To prepare RuO₂ NMs, RuCl₃ was used instead of AgNO₃ with other reactants and finally resulted in a black precipitate (Equation (2)). The products were heat-treated at 350 °C in a box furnace for 6 h and used for further catalyst preparation. The Ag₂O and RuO₂ NMs were loaded onto γ -Al₂O₃ on an ex situ basis at 0.5 and 1.0 wt.% and pelletized with a force of 8 ton per 1 cm diameter (with addition of a small amount of water). γ -Al₂O₃ is a conventional and commonly used commercial support, which is generally inert in nature. For the Ag₂O+RuO₂ composite, 0.5 wt.% each were loaded onto the γ -Al₂O₃ catalyst support by grinding the corresponding components using a pestle and mortar carefully for 1 h and the catalyst was then prepared. All catalyst-loaded pellets were heat-treated at 350 °C overnight (12 h), cut, and sieved in the range of 2–3 mm, and used further for CO oxidation experiments.

2.2. The CO Oxidation Experiment

The Ag₂O/ γ -Al₂O₃ (hereafter SLOAL) and (Ag₂O+RuO₂)/ γ -Al₂O₃ (hereafter referred to as SLORUOAL) catalysts were loaded (10 g) in the center of a tubular quartz reactor (having 1.5 cm diameter) with a catalyst volume of 11.5 cm³ (fixed bed). Then, the reactor was kept in a temperature furnace equipped with a temperature controller. The carbon monoxide gas flow rate was 2 cm³·min⁻¹, corresponding to 2000 ppm. The oxygen flow was fixed at 1.5 vol.%, and the N₂ gas was used as the remaining in the total of 1 L·min⁻¹. At the end of the 1 h reaction, the amount of CO conversion was measured in a Fourier transform infrared (FTIR) spectrometer (model: IFS 66/S spectrometer, Bruker, Billerica, MA, USA) fitted at the gas outlet. The percentage of CO oxidation was calculated as given in Equation (3).

The crystalline nature and product phase purity for the catalysts and SLO and SLORUO NMs were analyzed using a powder X-ray diffractometer (XRD, D/Max Ultima III diffractometer, Rigaku Corporation, Tokyo, Japan) equipped with Cu K_{α} radiation (wavelength, $\lambda = 0.154$ nm) operating at 40 mA and 40 kV. The morphology of the surface was analyzed with the help of a field emission scanning electron microscope (FESEM, JEM 1200 EX II, JEOL Ltd., Tokyo, Japan). The chemical nature of the catalyst surface was characterized using an X-ray photoelectron spectroscopy (XPS, model: ESCA 2000, VG Microtech, East Grinstead, UK) with monochromatic Mg K_{α} X-ray radiation (1253.6 eV) operated at 13 kV and 15 mA. The pass energy was 50 eV wide or 20 eV narrow, and the C1s (284.6 eV) was taken as a reference. The surface area and other pore characteristics of the catalysts were measured using Quantachrome Instruments (version 2.11, Boynton Beach, FL, USA). Thermal study by thermogravimetry analysis (TGA, STA7200, HITACHI, Tokyo, Japan) was carried out for the NMs and the catalysts. This study was performed by heating the sample from room temperature to 800 °C at a heating rate of 10 °C·min⁻¹ in N₂ atmosphere, and subsequent changes in weight were noted. For TPR analysis, 0.05 g of catalyst was first pre-treated using Ar gas (99.9%) at a heating rate of 10 °C·min⁻¹ from 25 to 300 °C and then kept at this high temperature for 30 min. Then, for H₂ reduction, the samples were heat-treated again from 30 to 500 $^{\circ}$ C in the presence of 5% H₂ + 95% Ar (total flow 30 sccm), and the TCD signals were collected as a function of temperature, which was a representation of the reducibility of the catalysts.

3. Results and Discussions

3.1. Crystallinity Studies of the NMs and Catalysts

The crystalline nature of SLO, SLORUO NMs, and the catalysts were studied using XRD spectroscopy, and the corresponding spectra are given in Figure 1. The prominent diffraction peaks observed for SLO at [20] 26.6, 32.8, 38.2, 44.4, 55.0, 57.5, 64.5, 68.7, and 77.3° represent (110), (111), (200), (211), (220), (221), (311), (222), and (123) crystal planes of cubic Ag₂O (JCPDS card No. 76-1393). The cell parameters are a = b = c = 4.76 Å, $\alpha = \beta = \gamma = 90^{\circ}$ and the space group is Pn $\overline{3}$ (201). Similarly, peaks referring to (110), (101), (200), (111), (210), (211), (220), (002), (310), (112), (301), and (202) planes of diffraction correspond to rutile-type RUO (JCPDS card No. 88-0322) with space group P42/mnm (136) (depicted in Figure S1). The SLORUO represented major diffraction peaks of Ag₂O and RuO₂ at its diffraction angle as observed separately for the corresponding NMs. The XRD spectra for the alumina catalyst support and the catalysts (1.0 wt.% loaded) are given in Figure 1 on the right side. The diffraction peaks observed at [20] 32.6, 37.2, 39.7, 45.7, 60.7, and 66.8°, represent (220), (311), (222), (400), (511), and (440) crystal planes of γ -Al₂O₃ (JCPDS card No. 50-0741) [11], and the small peak at 26.4° may correspond to the α -form. The NM-loaded catalyst also exhibited peaks similar to the catalyst support in which the metal oxide (silver and ruthenium oxide) peaks were not observed separately due to lower catalyst loading.



Figure 1. The X-ray diffraction spectrum observed for silver oxide (SLO), silver and ruthenium oxide (SLORUO) nanomaterials (NMs), catalyst support (γ -Al₂O₃, AL), and the catalysts (i.e., NMs loaded on catalyst support at 1.0 wt.%) are shown.

3.2. The Surface Morphological and Elemental Analysis

Figure 2 shows the FESEM surface morphological images of the SLO, RUO, and SLORUO NMs (a-c) and their energy dispersive X-ray elemental analysis results (d-f), respectively. The SLO NMs exhibited spherical aggregated structures with the size ranging from 200 nm to 1 µm. They contained 55.56 and 44.44 atomic percentage (at.%) of silver and oxygen and no other impurities were observed in the EDX spectrum (Figure 2a,d). The RUO NMs exhibited a mixture of major rod-like and small-sized spherical aggregates with rod sizes of 200 nm width and >2 μ m length. The EDX spectra showed 16.70 and 83.30 at.% of ruthenium and oxygen (Figure 2b,e, respectively). The presence of a strong peak at 2 keV observed in this sample is due to the long exposure of Pt coating used for FESEM analysis, which can be ignored. The SLORUO exhibited the presence of rod-like RUO and aggregated SLO. The atomic percentage of oxygen, ruthenium, and silver in this sample were found to be 75.77, 9.38, and 14.86, respectively (Figure 2c,f). The observed percentage of elements is, generally, a rough estimate due to tiny scan region and it depends on the catalyst dispersion. The FESEM and EDX analysis of the catalysts are shown in Figure S2. Since the catalyst contains majority of the catalyst support, locating the active catalyst morphology and diffraction peaks was not easy in FESEM and XRD, but they were detected in EDX spectra. As can be seen from the figure, the peaks that originated at 3.0 and 2.6 keV refer to the silver and ruthenium elements, respectively. Other peaks ratified the presence of oxygen and aluminum.



Figure 2. The field emission scanning electron microscopy surface morphological images of the SLO, RUO, and SLORUO NMs (**a**–**c**) and their energy dispersive X-ray elemental spectra (**d**–**f**), respectively.

3.3. The Surface Chemical Analysis of the Catalysts

The surface chemical nature of the catalysts was studied using XPS. The survey spectrum and core-level high-resolution spectra of Ag 3d, Al 2p, and O1s for SLOAL are given in Figure 3. The survey spectra showed the presence of aluminum, silver, oxygen, and adventitious carbon signals in their corresponding binding energy values. The Ag 3d exhibited two peaks at the binding energy (B.E.) values at 368.1 and 374.0 eV referring to Ag $3d_{\frac{5}{2}}^{\frac{5}{2}}$ and Ag $3d_{\frac{3}{2}}^{\frac{3}{2}}$ with doublet separation of 5.9 eV, which confirmed the formation of Ag₂O with no other oxidation states [12,13]. The Al 2p spectra of the γ -alumina support showed a singlet at the B.E. 74.4 eV [14]. The O 1s exhibited three peaks at B.E. values 529.9, 530.9, and 532.2 eV corresponding to oxygen in three environments. These are surface oxygen with silver (Ag₂O), oxygen in alumina (Al₂O₃), and oxygen in water (due to ambience) [12,15,16] (refer to Figure S3 for the XPS spectra for RUOAL). Figure 4 shows the survey and high-resolution, core-level XPS spectra for Ru 3d, Ag 3d, Al 2p, and O 1s of SLORUOAL. The presence of Ag, Ru, Al, and oxygen were confirmed from the survey spectrum. The Ru 3d and oxygen 1s spectra were deconvoluted using a Gauss-Laurentian peak-fitting program and fixed full-width half-maximum values. The deconvoluted peaks at the B.E. values 280.6 and 282.4 eV correspond to ruthenium in two kinds of oxidation states. One peak at 280.6 eV was confirmed as RuO₂, and regarding the other one confirmed at 282.4 eV, two interpretations of either hydrated RuO₂ or RuO₃ [17,18] were given [for reference: https://srdata.nist.gov/xps/selEnergyType.aspx]. At the same time, the RuO₂ phase was reported to be more stable in catalytic reactions and the presence of RuO₃ on RuO₂ was quite possible [19,20]. The two other peaks at 284.2 and 285.6 eV refer to carbon and oxidized carbon, since the Ru 3d and carbon-binding energies are closely located. The Ag 3d spectrum exhibited doublets correspond to Ag₂O. The B.E. at 74.7 eV observed for Al 2p corresponds to Al₂O₃. The O 1s spectrum showed a similar environment as observed in SLO in addition to the Ru-O_x (where x = 2 and 3 in most cases). The shift in the O 1s peak to lower binding energy in SLORUOAL as compared to SLOAL refers to the high affinity of NMs with a support, which is able to adsorb and dissociate oxygen molecules [11].



Figure 3. The XPS survey spectrum and core-level, high-resolution spectra for Ag 3d, Al 2p, and O1s observed for SLOAL.



Figure 4. The XPS survey spectrum and core-level high-resolution spectra for Ru 3d, Ag 3d, Al 2p, and O1s observed for SLORUOAL.

3.4. Thermal Stability of the NMs and Catalysts

The thermal stability of the NMs and catalysts were studied using thermogravimetry analysis (TGA). The weight loss corresponding to the component in the materials against incremental temperature was analyzed. This study also indicates the maximum temperature the catalysts or NMs can withstand in its original composition and reflects further changes after a certain range. Figure 5 shows the thermogram of SLO, SLOAL, SLORUO, and SLORUOAL. The SLO NMs showed three stage decompositions. The initial decomposition observed until 200 °C corresponds to the evaporation of surface moisture (water vapor). The other decomposition that occurred between 250 and 330 °C corresponds to the removal of remnant PEG. The final strong decomposition was between 350 and 420 °C and is related to the formation of metallic silver from Ag₂O [21]. In the thermal study from room temperature to 800 °C, about 5.9% weight loss was observed for SLO.



Figure 5. The TGA thermogram of the NMs and catalysts (at 1.0 wt.%).

The RUO (Figure S4) showed the removal of surface moisture, remnant PEG, and formation of metallic ruthenium at 200, until 600, and between 620 and 740 °C, respectively [22,23]. At the end of the experiment, RUO NMs lost 14.6% weight at 800 °C. In comparison to SLO, the RUO was more stable since metallic formation was observed at a higher temperature.

The SLORUO exhibited the cumulative behavior observed for SLO and RUO separately, but a notable point is that it showed only 8.4% weight loss at the end of the study. This means SLO had further increased the material stability of RUO by preventing further moisture absorption since RUO had a high affinity for water [17].

The catalysts (SLOAL and SLORUOAL) exhibited a gradually declining thermogram, major loss, which resulted due to moisture. Since the catalyst loading was only 1.0 wt.% in total and the remaining was the catalyst support (γ -Al₂O₃), determining decomposition due to catalyst-only seemed difficult. In addition, the catalyst support contains more pores and, thus, it might lead to more atmospheric water adsorption such that the total weight loss contribution at the end of the study is mainly from water. Other possible decomposition ranges for PEG and metallic formation are noted inside. The SLOAL and SLORUOAL showed good thermal stability with a loss of 5.6 and 7.6%, respectively.

3.5. Pore Statistics and Surface Area of the Catalysts

The surface area, pore volume, and pore diameter are some of the important parameters to understand the adsorbate–adsorbent interaction. The catalytic reaction is initiated by adsorption in the catalyst pores (acting as microreactors) followed by chemical (gaseous) reaction. The catalytic activity, moisture retention capacity, and catalyst shelf life are functions of the catalyst surface area. Changes in the isotherm shape during adsorption and desorption cycle would give the idea of the pore size of the catalyst and whether it is meso- or microporous, as given by Barrett–Joyner–Halenda (BJH) model.

The BET (Brunauer, Emmett, and Teller) model provides a suitable method for surface area analysis. In this model, gas adsorption (X) as a function of relative pressure $\left(\frac{P}{P0}\right)$ is measured and plotted using the following Equation (4), which is a straight line (the linearity indicates the strong interaction of the gas with catalyst) in general over the relative pressure of range 0.05–0.35.

$$\frac{1}{X\left[\left(\frac{P0}{P}\right)-1\right]} = \frac{1}{XmC} + \frac{C-1}{XmC}\left(\frac{P}{P0}\right)$$
(4)

where X_m is the number of atoms or molecules required to form a monolayer, $\left(\frac{P}{P0}\right)$ is the relative pressure, and C is a parameter related to heat of adsorption.

Figure 6 shows the adsorption–desorption isotherm (a–c) and multipoint BET plots (d–f) for the catalysts SLOAL, RUOAL, and SLORUOAL, respectively. The hysteresis shape of isotherm indicates that it belongs to type IV, which means the adsorption process on the mesoporous catalysts is performed through a multilayer adsorption and followed by capillary condensation. At a high pressure, the adsorption of the gas increases due to an increase in the number of open pores. The BET surface area (averaged after adsorption and desorption) and other pore characteristics are given in Table 1. The SLOAL and RUOAL showed the surface area of about 112.9 and 124.6 m²·g⁻¹, respectively. A relatively high surface area of RUOAL can accommodate more surface moisture and, thus, the greater weight loss observed in thermal study could be correlated. The SLORUOAL showed a surface area (96.5 m²·g⁻¹) that is actually lower in comparison to other catalysts, but a slightly higher pore diameter (8.2 nm).



Figure 6. The adsorption–desorption isotherm (**a–c**) and multipoint BET plots (**d–f**) corresponding to the catalysts SLOAL, RUOAL, and SLORUOAL at 0.5 wt.%, respectively. The pore size distribution graphs for the above samples given in Figure S5 show the pore diameter in the range of 3–10 nm.

Catalyst Name	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
SLOAL	112.9	0.23	7.98
RUOAL	124.6	0.24	7.89
SLORUOAL	96.5	0.19	8.17

Table 1. The surface area, pore volume and pore diameter of the catalysts (0.5 wt.%).

4. The CO Oxidation Performance of the Catalysts

The CO oxidation performance of the catalysts is depicted in Figure 7. The performance due to the effect of catalyst loading, such as 0.5 and 1.0 wt.% in dry (Figure 7a) and wet (Figure 7b) conditions using SLOAL, RUOAL and SLORUOAL, was studied.



Figure 7. The CO oxidation performances of the catalysts are shown. The performance due to the effect of catalyst loading, such as 0.5 and 1.0 wt.% in dry (**a**) and wet (**b**) conditions using SLOAL, RUOAL and SLORUOAL catalysts, respectively.

The onset of activities in dry conversion was observed at 100 °C for RUOAL whereas this was shown by SLOAL beyond 100 °C. Generally, the CO conversion efficiency was found to increase by increasing the temperature. Complete or 100% CO oxidation by 0.5 and 1.0 wt.% RUOAL was observed at 200 and 175 °C, respectively [7], while the SLOAL showed full oxidation at 300 and 350 °C for 0.5 and 1.0 wt.% loading, respectively. The SLORUOAL (made from 0.5% SLO and RUO each) exhibited full performance at 225 °C. In this activity region, silver catalyst was maintained in the stable Ag₂O state [24] lattice oxygen loss was possible since at 7% [8], which was negligible.

In wet conversion (i.e., with 1.5 vol.% H_2O), the total CO oxidation for 0.5 and 1.0 wt.% RUOAL was observed at 275 and 250 °C, respectively, while the 0.5 wt.% SLOAL showed full conversion at 525 °C, the 1.0 wt.% catalyst showed 84% up to 700 °C. At such a high temperature, the orientation of Ag (111) phase resulted in the lowest surface energy and decreased gas adsorption, diffusion, and direction of transport [25,26]. The SLORUOAL exhibited full oxidation at 275 °C. The reason for the higher temperature required in wet conversion, as compared to dry conversion, for total CO oxidation by catalysts is due to the competition between reactant gases and water molecules for adsorption in the catalyst pores [7]. In addition, an increase in catalyst loading from 0.5 to 1.0 wt.% in RUOAL sped up CO conversion and, thus, full conversion was achieved at a low temperature (25 °C difference), which is expected for a positive catalyst loading effect. However, in the case of SLOAL, increasing the catalyst loading decreased the CO oxidation performance. This required a higher temperature when the catalyst loading was increased from 0.5 to 1.0 wt.% (50 °C difference).

The experiment was conducted in a continuous mode for 7 h in order to analyze the stability of the catalysts. The temperature was fixed at 300, 175, and 200 °C for SLOAL, RUOAL, and SLORUOAL, respectively, and it was observed that the oxidation performance was not affected to significant extent.

In the literature, high-temperature activity due to silver was reported using 2.0 wt.% at 220 °C. Usually, catalytic activity of silver based catalysts depends on the surface architecture (related to gas transport), preparation method and pre-treatment conditions and medium (which influence the catalyst structure and electronic states, for example, through hydrogen reduction followed by oxidation). The activity may decrease due to the increase in the particle size, in which further decrease partially coordinated the active surface sites [27] in SLOAL as compared to RUOAL. Additionally, it showed that increasing silver loading increased the conversion percentage up to certain value and beyond that it tend to decrease [28,29]. It means that a small amount of silver loading resulted in better catalytic performance [30]. In addition, pre-treatment with O_2 at different temperature had shown different results (in that case the total flow was 30 sccm and with 0.25 g catalyst). Pre-treatment temperature until 500 °C for 8 wt.% Ag catalysts on SiO₂ support was reported as good activity [28] but its stability was not discussed. At the same time, the active sites of silver catalyst are considered an important parameter [31], which are generally oxygen atoms located at surface or subsurface [28]. Atomically, the Ag⁺ interacts more with oxygen atoms (Ag-O interaction) from gas phase and it is a chemisorption [32] reaction which is suitably a pseudo first order reaction observed using 5 wt.% Ag on silica [33] as the literature suggests. The mechanism of CO oxidation by silver or silver oxide is based on the ionic complex or charged cluster formation (Ag⁺-O⁻-CO⁻) since the CO is not adsorbed on the metallic silver (Ag^0) at room or higher temperature [31]. The formation of CO_2 and regeneration of silver oxide catalyst is given in Equations (5) and (6). This was shown as the rate determining the step [8].

$$Ag_2O + CO \rightarrow 2Ag + CO_2 \tag{5}$$

$$2Ag + O \rightarrow Ag_2O \tag{6}$$

When using Ag or Ag₂O as a catalyst, a slightly high-temperature performance was generally observed and influenced by catalyst support such as mesoporous silica or aluminum-incorporated mesoporous silica [34]. In addition, the mechanism related to catalytic activity of silver-based particles was previously detailed as Langmuir–Hinshelwood, Mars–van Krevelen, and Eley–Rideal, in which the molecular or atomic adsorption of species on the catalysts surface interacted in a slow stage [32]. In addition, CO being the reductive gas partially reduced the surface oxygen sites and the disappearance of oxygen species resulted in high-temperature operation [35], which can be confirmed from maximum wet CO oxidation performance at >500 °C in addition to competitive adsorption.

The well-known mechanism of CO oxidation by the RuO₂ surface is due to the adsorption and reaction of atomic oxygen species on the coordinative unsaturated Ru atoms and bridge position surface oxygen atoms as verified by Mars–van Krevelan [36]. The high catalytic activity at low temperature observed for RuO₂-based catalysts was due to the highly ordered mesoporous structure, edge and corner atoms of the 1-d rods and high surface area as confirmed by BET analysis (124.6 m²·g⁻¹).

In the case of SLORUOAL, understanding the mechanism between Ag and Ru oxide system needs more details. In bi-metallic catalyst (for example, Au–Ag), the activity was dependent on which of the above metal is more interactive with oxygen and also its nature or the amount of surface oxide [37]. However, in the present case, both SLO and RUO NMs were prepared separately, and the catalyst was prepared by external mixing (in order to maintain good dispersion and surface morphology but each component possibly still interacts) so that both could exhibit oxide states, thus enhancing the redox property, which was not observed but was somehow a shared performance [38]. With the addition of Ru-O, the high-temperature activity of Ag-O was altered to the low-temperature region, which is considered a positive effect. For example, the temperature programmed reduction profiles of the SLOAL, RUOAL, and SLORUOAL catalysts in Figure 8 showed the H₂ consumption of 0.037, 0.046, and 0.050 mmol·g⁻¹ with peak areas 66.04, 76.15, and 83.295, respectively. This indicated the reduction behavior and dispersion of the catalysts. Three peak regions were observed for SLOAL such as 100–220 °C, around 300 °C, and T_{max} at around 380 °C. Those peaks corresponded to the reduction of small-sized silver oxides and well-dispersed oxide phases [39] and the T_{max} represents the reduction of the bulk oxide phase (from Ag₂O to metallic Ag) of the sample, which is size dependent (bigger particle size for SLOAL). For RUOAL, the low-temperature peak at 150 °C and high-temperature peaks at 200 and 370 °C represent the reduction of surface RuO₂ crystallite [40], small-sized particles, and bulk reductions of rod structures [7], respectively. The mixed catalyst exhibited a shift in the peak towards lower temperature and a slight shift to high temperature as compared to RUOAL. Even though a small increase in the peak area was noted for SLORUOAL as compared to RUOAL, which is an indication of better dispersion, the CO oxidation performance was slightly low in comparison to RUOAL, and the mixed performance seemed to be due to lower surface area.



Figure 8. The temperature-programmed reduction profiles for the SLOAL, RUOAL, and SLORUOAL catalysts.

5. Conclusions

This research dealt with the synthesis, characterization, and carbon monoxide (CO) oxidation performance of silver oxide and its composite made with ruthenium oxide. The wet chemically prepared SLO and SLORUO exhibited spherical aggregates and rod-like surface morphology. The XRD spectra showed cubic and mixed (cubic and rutile) structures for SLO and SLORUO, respectively. The SLO and RUO were in the Ag₂O and RuO₂ chemical states as analyzed using XPS. The thermal stability of SLO was good until 350 °C, and lost only 5.9% of the total mass at the end of 800 °C heat test. A similar trend was noted for SLORUO, but the weight loss was 8.4% at 800 °C. The SLO and SLORUO NMs were loaded onto γ -Al₂O₃ support at 0.5 and 1.0 wt.% and used for thermal CO oxidation experiments, which showed surface area values of about 113 and 97 m²·g⁻¹, respectively. The dry CO conversion using SLO showed concentration-dependent behavior in which the temperature required for full CO conversion was increased by increasing concentration. The SLOAL showed full oxidation at 300 and 350 °C for 0.5 and 1.0 wt.% loading, respectively, due to the slow adsorption and reaction on the surface by reactant molecules. At the same time, the complete CO conversion by SLORUO was observed at 225 and 250 °C in dry and wet conditions. The TPR profiles of the SLOAL and SLORUOAL catalyst showed the hydrogen consumption of 0.037 and 0.050 mmol·g⁻¹ with peak areas of 66.04 and 83.295, respectively. Though the SLO exhibited high-temperature performance, combining it with RUO enhanced its catalytic activity at low temperature and vice versa. The reason was due to catalyst loading, structure (as rods have edge and corners), surface area, and the complex metal oxygen interaction of catalysts with molecular CO. Thus, this research attempted to investigate the use of silver oxide as a low-temperature catalyst by the addition of RuO_2 .

Supplementary Materials: The following are available online at http://www.mdpi.com/2571-9637/3/2/19/s1, Figure S1: The XRD spectrum of ruthenium oxide (RUO) NMs, Figure S2: The FESEM and EDX analysis of the catalysts (1.0 wt.%) are given, Figure S3: The XPs survey spectrum, core level high-resolution spectra for Ru 3d, O1s and Al 2p observed for the RUOAL are given, Figure S4: The TGA thermogram of RUO NMs, Figure S5: The pore size distribution graphs for the catalysts are given which shows the pore diameter in the range of 3-10 nm.

Author Contributions: A.A.: Performed the experiments, writing and editing the manuscript. R.H.J.: Measurement of TGA and FESEM. J.-H.B.: Managing the whole experimental processes and given advices on manuscript preparation. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Basic Science Research Program through the NRF funded by the Ministry of Education (NRF-2018R1D1A1B07051012), Korea.

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

References

- Manikandan, V.; Velmurugan, P.; Park, J.-H.; Chang, W.-S.; Park, Y.-J.; Jayanthi, P.; Cho, M.; Oh, B.-T. Green synthesis of silver oxide nanoparticles and its antibacterial activity against dental pathogens. *3 Biotech* 2017, 7, 72–80. [CrossRef]
- 2. Ananth, A.; Dharaneedharan, S.; Gandhi, M.S.; Heo, M.-S.; Mok, Y.S. Novel RuO₂ nanosheets—Facile synthesis, characterization and application. *Chem. Eng. J.* **2013**, *223*, 729–736. [CrossRef]
- 3. Yan, Y.; Wang, T.; Li, X.; Pang, H.; Xue, H. Noble metal-based materials in high-performance supercapacitors. *Inorg. Chem. Front.* **2017**, *4*, 33–53. [CrossRef]
- Hong, S.-C.; Kim, S.; Jang, W.-J.; Han, T.-H.; Hong, J.-P.; Oh, J.-S.; Hwang, T.; Lee, Y.; Lee, J.; Nam, J.-D. Supercapacitor characteristics of pressurized RuO₂/carbon powder as binder-free electrodes. *RSC Adv.* 2014, 4,48276–48284. [CrossRef]
- Lu, C.A.; Lin, P.; Lin, H.-C.; Wang, S.-F. Effects of Silver Oxide Addition on the Electrical Resistivity and Microstructure of Low-Temperature-Curing Metallo-Organic Decomposition Silver Pastes. *Jpn. J. Appl. Phys.* 2007, 46, 4179–4183. [CrossRef]
- Liu, Z.-P.; Hu, P. Mechanism for the high reactivity of CO oxidation on a ruthenium–oxide. *J. Chem. Phys.* 2001, 114, 5956–5957. [CrossRef]
- Ananth, A.; Gregory, D.H.; Mok, Y.S. Synthesis, Characterization and Shape-Dependent Catalytic CO Oxidation Performance of Ruthenium Oxide Nanomaterials: Influence of Polymer Surfactant. *Appl. Sci.* 2015, 5, 344–358. [CrossRef]
- 8. Imamura, S.; Sawada, H.; Uemura, K.; Ishida, S. Oxidation of Carbon Monoxide Catalyzed by Manganese-Silver Composite Oxides. *J. Catal.* **1988**, *109*, 198–205. [CrossRef]
- 9. Taylor, S.H.; Rhodes, C. Ambient temperature oxidation of carbon monoxide using a Cu₂Ag₂O₃ catalyst. *Catal. Lett.* **2005**, *101*, 31–33. [CrossRef]
- Chen, L.; Ma, D.; Pietruszka, B.; Bao, X. Carbon-Supported Silver Catalysts for CO Selective Oxidation in Excess Hydrogen. J. Nat. Gas Chem. 2006, 15, 181–190. [CrossRef]
- 11. Wang, H.; Luo, S.; Li, X.; Liu, W.; Wu, X.; Weng, D.; Liu, S. Thermally stable Ag/Al₂O₃ confined catalysts with high diffusion-induced oxidation activity. *Catal. Today* **2019**, *332*, 189–194. [CrossRef]
- 12. Gerenser, L.J. Photoemission investigation of silver/poly (ethylene terephthalate) interfacial chemistry: The effect of oxygen-plasma treatment. *J. Vac. Sci. Technol. A* **1990**, *8*, 3682. [CrossRef]
- Tjeng, L.H.; Meinders, M.B.J.; van Elp, J.; Ghijsen, J.; Sawatzky, G.A. Electronic structure of Ag₂O. *Phys. Rev. B* 1990, 41, 3190–3199. [CrossRef] [PubMed]
- 14. Hess, A.; Kemnitz, E.; Lippitz, A.; Unger, W.E.S.; Menz, D.H. ESCA, XRD, and IR characterization of aluminum oxide, hydroxyfluoride, and fluoride surfaces in correlation with their catalytic activity in heterogeneous halogen exchange reactions. *J. Catal.* **1994**, *148*, 270–280. [CrossRef]
- 15. Wagner, C.D.; Passoja, D.E.; Hillery, H.F.; Kinisky, T.G.; Six, H.A.; Jansen, W.T.; Taylor, J.A. Auger and photoelectron line energy relationships in aluminum-oxygen and silicon-oxygen compounds. *J. Vac. Sci. Technol.* **1982**, *21*, 933. [CrossRef]
- 16. Venezia, A.M.; Bertoncello, R.; Deganello, G. X-ray photoelectron spectroscopy investigation of pumice-supported nickel catalysts. *Surf. Interface Anal.* **1995**, *23*, 239–247. [CrossRef]

- 17. Morgan, D.J. Resolving ruthenium: XPS studies of common ruthenium materials. *Surf. Interface Anal.* **2015**, 47, 1072–1079. [CrossRef]
- 18. Selvaganesh, S.V.; Selvarani, G.; Sridhar, P.; Pitchumani, S.; Shukla, A.K. A Durable RuO₂-Carbon-Supported Pt Catalyst for PEFCs: A Cause and Effect Study. *J. Electrochem. Soc.* **2012**, *159*, B463–B470. [CrossRef]
- 19. Farkas, A.; Mellau, G.C.; Over, H. Novel Insight in the CO Oxidation on RuO₂ (110) by in Situ Reflection-Absorption Infrared Spectroscopy. *J. Phys. Chem. C* 2009, *113*, 4341–14355. [CrossRef]
- 20. Bianchi, C.L.; Ragaini, V.; Cattania, M.G. An XPS study on ruthenium compounds. *Mater. Chem. Phys.* **1991**, 29, 297–306. [CrossRef]
- 21. Taufik, A.; Saleh, R. The Influence of Graphene on Silver Oxide Synthesis Through Microwave Assisted Method. *AIP Conf. Proc.* **2018**, 2023, 020018–020021.
- 22. Ananth, A.; Mok, Y.S. Dielectric Barrier Discharge (DBD) Plasma Assisted Synthesis of Ag₂O Nanomaterials and Ag₂O/RuO₂ Nanocomposites. *Nanomaterials* **2016**, *6*, 42. [CrossRef]
- Yuan, C.; Chen, L.; Gao, B.; Su, L.; Zhang, X. Synthesis and utilization of RuO₂.xH₂O nanodots well dispersed on poly (sodium 4-styrene sulfonate) functionalized multi-walled carbon nanotubes for supercapacitors. *J. Mater. Chem.* 2009, 19, 246–252. [CrossRef]
- 24. Garner, W.E.; Reeves, L.W. The thermal decomposition of silver oxide. *Trans. Faraday Soc.* **1954**, *50*, 254–260. [CrossRef]
- Nagy, A.J.; Mestl, G.; Herein, D.; Weinberg, G.; Kitzelmann, E.; Schlogl, R. The Correlation of Subsurface Oxygen Diffusion with Variations of Silver Morphology in the Silver–Oxygen System. *J. Catal.* 1999, 182, 417–429. [CrossRef]
- 26. Li, W.-X.; Stampfl, C.; Scheffler, M. Insights into the function of silver as an oxidation catalyst by ab initio, atomistic thermodynamics. *Phys. Rev. B* 2003, *68*, 165412–165427. [CrossRef]
- 27. Khan, I.A.; Sajid, N.; Badshah, A.; Wattoo, M.H.S.; Anjum, D.H.; Nadeem, M.A. CO Oxidation Catalyzed by Ag Nanoparticles Supported on SnO/CeO₂. *J. Braz. Chem. Soc.* **2015**, *26*, 695–704. [CrossRef]
- 28. Zhang, X.; Qu, Z.; Li, X.; Wen, M.; Quan, X.; Ma, D.; Wu, J. Studies of silver species for low-temperature CO oxidation on Ag/SiO₂ catalysts. *Sep. Pur. Technol.* **2010**, *72*, 395–400. [CrossRef]
- 29. Li, G.; Zhang, X.; Feng, W.; Fang, X.; Liu, J. Nanoporous CeO₂-Ag catalysts prepared by etching the CeO₂/CuO/Ag₂O mixed oxides for CO oxidation. *Corros. Sci.* **2018**, *134*, 140–148. [CrossRef]
- Gardner, S.D.; Hoflund, G.B. Catalytic Behavior of Noble Metal/Reducible Oxide Materials for Low-Temperature CO Oxidation. 1. Comparison of Catalyst Performance. *Langmuir* 1991, 7, 2135–2139. [CrossRef]
- Kolobova, E.; Pestryakov, A.; Shemeryankina, A.; Kotolevich, Y.; Martynyuk, O.; Vazquez, H.J.T.; Bogdanchikova, N. Formation of silver active states in Ag/ZSM-5 catalysts for CO oxidation. *Fuel* 2014, *138*, 65–71. [CrossRef]
- 32. Dey, S.; Dhal, G.C. Applications of silver nanocatalysts for low-temperature oxidation of carbon monoxide. *Inorg. Chem. Commun.* **2019**, *110*, 107614–107625. [CrossRef]
- Lachkov, P.T.; Chin, Y.-H.C. Catalytic Consequences of Reactive Intermediates during CO Oxidation on Ag Clusters. ACS Catal. 2018, 8, 11987–11998. [CrossRef]
- 34. Qu, Z.; Zhang, X.; Yu, F.; Liu, X.; Fu, Q. Role of the Al chemical environment in the formation of silver species and its CO oxidation activity. *J. Catal.* **2015**, *321*, 113–122. [CrossRef]
- 35. Gac, W. The influence of silver on the structural, redox and catalytic properties of the cryptomelane-type manganese oxides in the low-temperature CO oxidation reaction. *Appl. Catal. B Environ.* **2007**, 75, 107–117. [CrossRef]
- Park, J.-N.; Shon, J.K.; Jin, M.; Kong, S.S.; Moon, K.; Park, G.O.; Boo, J.H.; Kim, J.M. Room-temperature CO oxidation over a highly ordered mesoporous RuO₂ catalyst. *Reac. Kinet. Mech. Catal.* 2011, 103, 87–99. [CrossRef]
- Iizuka, Y.; Hiragi, Y.; Yakushiji, H.; Miura, T. An examination of active sites on Au-Ag bimetallic catalysts based on CO oxidation over Au/Ag₂O and a comparison to Ag-contaminated Au powder. *Chin. J. Catal.* 2016, *37*, 1712–1720. [CrossRef]
- Li, L.; Yang, Q.; Zhang, C.; Yan, J.; Peng, Y.; Li, J. Hollow-Structural Ag/Co₃O₄ Nanocatalyst for CO Oxidation: Interfacial Synergistic Effect. ACS Appl. Nano Mater. 2019, 2, 3480–3489. [CrossRef]

- 39. Khan, Z.; Dummer, N.F.; Edwards, J.K. Silver–palladium catalysts for the direct synthesis of hydrogen peroxide. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2018**, *376*, 20170058. [CrossRef]
- 40. Xu, X.; Liu, F.; Huang, J.; Luo, W.; Yu, J.; Fang, X.; Lebedeva, O.E.; Wang, X. The Influence of RuO₂ Distribution and Dispersion on the Reactivity of RuO₂-SnO₂ Composite Oxide Catalysts Probed by CO Oxidation. *ChemCatChem* **2019**, *11*, 2473–2483. [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/).