Research Article

Effect of Au Precursor and Support on the Catalytic Activity of the Nano-Au-Catalysts for Propane Complete Oxidation

Arshid M. Ali,¹ Muhammad A. Daous,¹ Ahmed Arafat,¹ Abdulraheem A. AlZahrani,¹ Yahia Alhamed,¹ Turdimuhammad Abdullah,¹ and Lachezar A. Petrov²

¹Department of Chemical and Materials Engineering, Faculty of Engineering, King Abdulaziz University, Jeddah 21589, Saudi Arabia

²SABIC Chair of Catalysis, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Correspondence should be addressed to Arshid M. Ali; amsali@kau.edu.sa

Received 26 May 2015; Revised 1 November 2015; Accepted 4 November 2015

Academic Editor: Sherine Obare

Copyright © 2015 Arshid M. Ali et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Catalytic activity of nano-Au-catalyst(s) for the complete propane oxidation was investigated. The results showed that the nature of both Au precursor and support strongly influences catalytic activity of the Au-catalyst(s) for the propane oxidation. Oxidation state, size, and dispersion of Au nanoparticles in the Au-catalysts, surface area, crystallinity, phase structure, and redox property of the support are the key aspects for the complete propane oxidation. Among the studied Au-catalysts, the Au_{H₂AuCl₄}-Ce catalyst is found to be the most active catalyst.

1. Introduction

VOCs are a wide range of chemical compounds emitted from both chemical and petrochemical process industries [1–3]. According to US Environmental Protection Agency (EPA), more than 300 chemical compounds are VOCs [1]. Most of the VOCs exhibited similar behavior in the atmosphere in spite of the fact that both physical and chemical properties of these compounds are very different from each other [4]. Emission of VOCs into atmosphere causes serious air pollution and environmental issues such as stratospheric ozone depletion, formation of ground level ozone, photochemical smog, and aggravation of the global greenhouse effect [4–7]. Henceforth, low cost, effective, and efficient reduction of VOCs is still one of the main challenges in chemical and industrial processes [1].

Among the applied methods, catalytic oxidation is so far the most efficient method for the abatement of VOCs at low cost [8]. This method is not limited by concentration, even very low concentrated VOCs (<1%) could be eliminated [2]. Also, catalytic oxidation requires much lower temperature than the conventional thermal incineration. Additionally, instead of transferring the pollutant compounds to another

phase, complete oxidation of VOC could be achieved by using catalytic oxidation processes [9].

Platinum and palladium catalysts were widely used for the oxidation of VOCs [9–11]. Recent studies showed that because of higher activity, better selectivity, and comparatively lower cost as to that of platinum and palladium, the Au-catalysts are expected to have practical application for the removal of VOCs [12, 13].

The catalytic performance of the Au containing catalysts depends on the size of the gold, its oxidation state, physical and chemical properties of the support [14–18], and surface morphology.

Many studies [19–23] had shown that Au-catalysts properties are very sensitive to the catalyst preparation protocols such as pH of the liquid media [24–27], temperature of precipitation of gold, used precipitating agent [28–30], and calcination temperature [14, 31–34].

Usually, in the preparation of Au-catalysts, chloroauric acid is used as Au precursor. Several other Au precursors, such as Au(PPh₃)(NO)₃ and Au acetate, were also used for the preparation of Au-catalysts [35–37]. However, until now, the aspects of the influence of Au precursors on the catalytic activity of Au-catalysts have not been studied systematically.

TABLE 1: Summary of the prepared catalysts.

Composition	Precursor	Nomenclature
1% Au-CeO ₂	Chloroauric acid trihydrate	Au _{H₃AuCl₄} -Ce
1% Au-ZrO ₂	Chloroauric acid trihydrate	Au _{H₃AuCl₄} -Zr
1% Au-75% CeO ₂ -25% ZrO ₂	Chloroauric acid trihydrate	Au _{H₃AuCl₄} -Ce-Zr
1% Au-CeO ₂	Gold (III) bromide	Au _{AuBr₃} -Ce
1% Au-CeO ₂	Gold monoiodide	Au _{AuI} -Ce

None of the published studies is yet reported on the effect of Au precursor on the catalytic activity of the Au-catalysts for the complete oxidation of propane.

At this moment there is no clear understanding regarding which oxidation state of Au atoms (either Au⁺¹ or Au⁺³) is more active in the reactions by using gold catalysts [34, 38–41]. Based on the available literature, it is estimated that based on different Au valence states in the different Au precursors, the Au oxidation state in different catalyst will differ and we might be able to prepare catalyst with beforehand defined properties.

In this study, effect of CeO₂ and ZrO₂ supports and different Au halogen containing precursors, such as H₃AuCl₄·3H₂O, AuBr₃, and AuI, on the catalytic activity of Au-catalysts for the complete oxidation of propane is investigated and were characterized by using a wide range of analytical techniques, such as XRD, XPS, TEM, TPR, and BET.

2. Experimental

2.1. Materials. The following chemical materials were used for the preparation of the Au-catalyst (as summarized in Table 1): potassium hydroxide (KOH) 86%, Fluka; nitric acid (HNO₃) 69%, UN 2013; magnesium citrate (C₁₂H₁₀Mg₃O₁₄·9H₂O) 95%, Fluka; cerium oxide (CeO₂) 99.90%, Acros; zirconium oxide (ZrO₂) 99.90%, Aldrich; chloroauric acid (H₃AuCl₄) 99.95%, Acros; Au bromide (AuBr₃) 99.95%, Acros; and Au iodide (AuI) 99.95%, Acros. Both stock and reagent solutions were prepared by using deionized water.

2.2. Catalyst Preparation. The Au-catalysts were prepared in two steps: (i) preparation of the single and double oxide support and (ii) Au deposition-precipitation.

2.3. Support Preparation. Accurately weighed amounts of each oxide, CeO₂ and ZrO₂, and double oxide mechanical mixture of 7.5 gms CeO₂ and 2.5 gm ZrO₂ were ultrasonically treated for 1 h in a Power Sonic 410 instrument at a high sonication frequency at room temperature. Lastly, the well-treated catalyst support was dried at 120°C in an oven for 2 h before using it for the Au deposition step.

2.4. Au Deposition on Support. The deposition-precipitation of Au on support was carried out in a Mettler Toledo Labmax reactor, which permits the precise control of the pH, temperature, liquid reagent delivery, and mixing of the suspension. First, 13.5 cm³ of 0.1 M KOH and 3.86 cm³ of DIW per gram

of the freshly prepared support were added to a Labmax reactor flask and mixed at room temperature at 180 rpm at pH 12.7. The reactor temperature was raised to 60°C over 10 min before adding the precisely calculated amount of 1% Au in 10 cm³ DIW using different gold precursors (H₃AuCl₄·3H₂O, AuBr₃ and AuI) as the Au source. Very soon after the addition of Au, the pH was decreased first to 10.4 and then to 8 within the next 5 min using consecutively 0.5 M and 0.1 M HNO₃. The ageing of the catalyst was carried by adding specified amounts of the Mg-citrate solution. The system was aged for 1 h at 60°C and 180 rpm.

The freshly prepared sludge was rinsed multiple times with lukewarm DIW under vacuum. The removal of chloride ions was ensured using AgNO₃ test. Then the catalytic mass was dried for 4 h and calcined at 525°C for 4 h in air. The catalyst grains (250–500 μm) were then prepared by grinding the pelletized catalytic mass. The details of the three different types of prepared catalysts are summarized in Table 1.

2.5. Catalytic Activity Test. Catalytic activity experiments for the complete oxidation of propane were carried in a PID Microactivity Reference reactor system. The reaction mixture at reactor inlet contained 0.5 vol% propane in He. All of the catalytic tests were carried out in a 4 mm diameter quartz glass reactor charged with 0.5 g of the catalyst at temperatures range from 30 to 450°C at 24000 h⁻¹ GHSV. In each experiment, the temperature was increased in 15°C steps at a ramping rate of 10°C/min. The steady-state regime at each temperature was achieved after 45 min.

The gas flow rates were controlled by Bronkhorst mass flow controllers with an accuracy of 0.1% of the fixed value. The temperature was kept constant within 0.5°C and monitored throughout the catalytic experiment using PID Microactivity Reference software.

The reaction products were periodically analysed using an intermittently connected GC. Three analyses of reaction products were recorded for each reaction condition to monitor the repeatability of the experimental measurements. In addition, all of the catalysts were used at least twice to check the reproducibility and were found to be highly reproducible (standard variance ± 1.0) under the set parameters of the PID Microactivity apparatus.

Water and CO₂ were the only products of the oxidation reaction at the reactor outlet in all experiments. An Agilent 7890A GC system equipped with a flame ionisation detector (FID) and thermal conductivity detector (TCD) was used to identify and monitor reaction end products. Data processing was performed using GC ChemStation B.04.03. A 0.5-cm³ gas

sample, Agilent DBI/122-1063 (1 μm , 60 m $\times$ 0.25 mm) and HayeSep Q (2.4 m) columns, and He and N₂ carrier gases were used for FID and TCD, respectively.

2.6. Catalyst Characterization. Temperature programmed reduction (TPR) studies were conducted on ChemBET Pulsar TPD/TPO/TPR (Quantachrome). The well-purged sample was reduced by flow of 5% H₂ in N₂ at constant flow rate of 15 mL/min in the temperature range of 40–650°C.

Pore volume and surface area of the support and catalysts were measured by Quantachrome Nova 2000 and Quantachrome Pore Master instrument by mercury porosimetry method. In the pore master instrument, 0.4 g of sample was first loaded in low-pressure station to fill the mercury into sample at 3.5 atm. The sample cell was then loaded in high-pressure station for mercury intrusion at up to 4200 atm and followed extrusion to ambient pressure. The results were obtained by using Quantachrome Pore Master instrument software.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out in an ultra-high vacuum multitechnique surface analysis system (SPECS GmbH, Germany) at base pressure of 10^{−10} bar range. A standard dual anode X-ray source SPECS XR-50 with Mg-K α , 1283.6 eV, was used to irradiate the sample surface with 13.5 kV and 100 W and with take-off angle for electrons at 90° relative to sample surface plane. As the standard practice in XPS studies, the adventitious hydrocarbon C1s line (284.6 eV) corresponding to C-C bond has been used as binding energy reference for the charge correction.

X-ray powder diffraction (XRD) patterns were recorded by using INEL CPS 180 powder diffractometer EQUINOX 1000 system. Filtered Co K α 1 radiation was used to irradiate the sample with 30 kV and 30 mA. Routine spectra were recorded with 2 θ (10 to 110°) with a step size of 0.029°. The powder pattern analyses were processed by using Match© software for phase identification with both COD and ICDD databases, IMAD-INEL© data processing software was used for graphical illustrations, and MAUD© software was used for Rietveld analysis method.

3. Results and Discussion

3.1. Catalytic Activity

3.1.1. Effect of the Support. Figure 1 provides the catalytic activity data for all the Au-catalysts Au_{H_{Au}Cl₄}-Ce, Au_{H_{Au}Cl₄}-Zr, and Au_{H_{Au}Cl₄}-Ce-Zr as well as for their supports CeO₂ and ZrO₂ and the CeO₂-ZrO₂ mixture.

All the supports have low catalytic activity. Under the same reaction conditions, the CeO₂ has shown the highest catalytic activity as compared to the other two, ZrO₂ and CeO₂-ZrO₂ samples. At 400°C, over CeO₂ around 40% of the propane was oxidized. While at same reaction temperature and GHSV, over the ZrO₂ propane conversion was less than 5%.

The catalytic activity of the CeO₂-ZrO₂ mixture was between activities of the CeO₂ and ZrO₂. At 400°C nearly

FIGURE 1: Comparison of the catalytic activity of the supports, Au_{H_{Au}Cl₄}-Ce catalyst, Au_{H_{Au}Cl₄}-Zr catalyst, and Au_{H_{Au}Cl₄}-Ce-Zr catalyst at GHSV 24000 h^{−1}.

10% of the propane was oxidized. However, the mixture of both ZrO₂ and CeO₂ had shown increased catalytic activity at temperatures above 400°C in comparison to ZrO₂ alone, which is because of the presence of CeO₂. Therefore, CeO₂, because of its high catalytic activity, is found to be the best support for preparation of Au-catalysts for propane oxidation and it was used in our further studies.

The catalytic activities of the three Au-catalysts Au_{H_{Au}Cl₄}-Ce, Au_{H_{Au}Cl₄}-Zr, and Au_{H_{Au}Cl₄}-Ce-Zr were higher than the catalytic activities of the corresponding supports. Among the Au-catalysts, the Au_{H_{Au}Cl₄}-Ce catalyst was found to have the highest activity for complete propane oxidation at lower temperature and 50% conversion of propane was achieved at around 410°C. For the other two Au-catalysts Au_{H_{Au}Cl₄}-Ce-Zr and Au_{H_{Au}Cl₄}-Zr, the 50% conversions were achieved at higher temperatures of 450°C and 510°C, respectively. Au_{H_{Au}Cl₄}-Ce-Zr sample is more active than the Au_{H_{Au}Cl₄}-Zr, and the catalytic activity of Au_{H_{Au}Cl₄}-Ce-Zr is higher than catalytic activity of the Au_{H_{Au}Cl₄}-Zr. Difference between catalytic activity of Au_{H_{Au}Cl₄}-Zr and ZrO₂ is very large as compared to the other support and respective Au-catalyst.

The results suggested that the interaction of Au with different catalytically active support is different. In order to investigate the effect of the Au precursor, Au-catalysts obtained from three different Au precursors on highly active support CeO₂ were catalytically tested and results are discussed in next sections.

3.1.2. Effect of the Au Precursor. Figure 2 shows the catalytic activity comparison of the three Au-catalysts (Au_{H_{Au}Cl₄}-Ce, Au_{AuBr₃}-Ce, and Au_{AuI}-Ce) prepared by using three different Au precursors H_{Au}Cl₄·3H₂O, AuBr₃, and AuI on the support CeO₂.

TABLE 2: Textural properties of the gold catalysts and the support.

Gold catalysts	Surface area (m ² /g) ^a	Phase structure ^b	Particle size of gold ^c	Crystal size (nm) ^b	
				CeO ₂	ZrO ₂
CeO ₂	131.1	Fluorite cubic		22	
Au _{H AuCl₄} -Ce	132.0	Fluorite cubic	~5 nm	23	
Au _{AuBr₃} -Ce	128.0	Fluorite cubic	~14 nm	24	
Au _{AuI} -Ce	126.7	Fluorite cubic	17 nm	24	
ZrO ₂	80.0	Amorphous			70
Au _{H AuCl₄} -Zr	80.3	Amorphous	—		72
Ce-Zr	118.0	Fluorite cubic		24	24
Au _{H AuCl₄} -Ce-Zr	120.1	Fluorite cubic	—	20	26

^aObtained by N₂ adsorption; ^bobtained by XRD; ^cobtained by STEM.

FIGURE 2: Catalytic activity comparison of the Au_{H AuCl₄}-Ce catalyst, Au_{AuBr₃}-Ce catalyst, and Au_{AuI}-Ce catalyst prepared by using three different gold precursors at GHSV 24000 h⁻¹.

The Au-catalysts prepared from different Au precursor have shown different catalytic activity. The Au_{H AuCl₄}-Ce catalyst has the highest catalytic activity (nearly 100% conversion at 450°C) in comparison to the other two catalysts Au_{AuBr₃}-Ce and Au_{AuI}-Ce. The lowest catalytic activity was registered for Au_{AuBr₃}-Ce: 50% conversion of propane was achieved at 520°C. Catalytic performance of the Au_{AuI}-Ce was slightly better than that of Au_{AuBr₃}-Ce: nearly 60% conversion of propane was obtained at 520°C.

Interestingly, the catalytic activity order of all the Au-catalysts obtained from different Au precursor follows the same trends as the solubility constant K_{sp} of each Au precursor. The solubility constants K_{sp} values of the three Au precursors are 7.9×10^{-5} for $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 1.6×10^{-23} for AuI , and 4.0×10^{-36} for AuBr_3 [42]. The K_{sp} value of AuI is higher than that of AuBr_3 which exactly correlates with the order of activities of the catalysts prepared from AuI and AuBr_3 precursors.

Based on the catalytic activity and K_{sp} data, the highest catalytic activity of the Au_{H AuCl₄}-Ce catalyst could be the result of the highest K_{sp} value of HAuCl_4 that could have led to the better Au dispersion, an important aspect for the higher catalytic activity of the Au-catalyst.

In order to further investigate the role of different Au precursor to the Au-catalysts, detailed XRD, XPS, TPR, TEM, and BET analyses were also performed. The obtained results are summarized in the following sections.

3.2. Textural Property of the Au-Catalysts. It is widely accepted that high surface area is very important in enhancing the catalytic activity of the Au-catalyst [43, 44]. As listed in Table 2, among three different supports, CeO₂ has the highest surface area and the most effective support to enhance catalytic activity of Au-catalysts, whereas ZrO₂ has shown least surface area and lowest catalytic activity among the supports. Surface area of CeO₂-ZrO₂ was found to be in between CeO₂ and ZrO₂, which is well corresponded to its catalytic activity. In summary, the observed catalytic activity of the supports is directly correlated with their surface area.

In few studies [45–47], it is reported that physical structure, crystal size, and crystalline form of the catalysts could be one of the key reasons governing the catalytic activity of Au-catalysts. As shown in Table 2, well-defined fluorite cubic structure was observed for CeO₂ and CeO₂-ZrO₂ and for corresponding Au-catalysts. In addition, smaller crystal size was observed for these catalysts (20–25 nm). While for ZrO₂ and Au_{H AuCl₄}-Zr catalyst, part of the ZrO₂ is amorphous and crystal size of the rest of the ZrO₂ was found to be considerably large (above 70 nm). This result indicates that textural properties of the supports have significant effect on enhanced catalytic activity of the Au-catalysts.

From the XRD pattern (as shown in Figure 3), it was observed that the XRD peak positions of Au-catalysts are nearly similar to the peaks of corresponding supports. The XRD peak for Au species, supposed to appear at around 38° and 44° [48], did not appear. This could be because of the following two reasons:

- The Au particles were dispersed very well on the surface of the supports and the particles size might be very small [48–50].

TABLE 3: The oxidation states of gold in in $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst, $\text{Au}_{\text{AuBr}_3}$ -Ce catalyst, Au_{AuI} -Ce catalyst, $\text{Au}_{\text{HAuCl}_4}$ -Zr catalyst, and $\text{Au}_{\text{HAuCl}_4}$ -Ce-Zr catalyst obtained by deconvolution of Au 4f peaks.

Catalyst	Gold oxidation state
$\text{Au}_{\text{HAuCl}_4}$ -Ce	Au^{+1} , Au^{+3}
$\text{Au}_{\text{AuBr}_3}$ -Ce	Au^{+3} , Au^{-}
Au_{AuI} -Ce	Au^{+1}
$\text{Au}_{\text{HAuCl}_4}$ -Zr	Au^{+1}
$\text{Au}_{\text{HAuCl}_4}$ -Ce-Zr	Au^{+1} , Au^{+3}

FIGURE 3: XRD pattern of the supports, $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst, $\text{Au}_{\text{HAuCl}_4}$ -Zr catalyst, and $\text{Au}_{\text{HAuCl}_4}$ -Ce-Zr catalyst at GHSV 24000 h^{-1} .

- (ii) It could be because Au loading is beyond the XRD lower sensitivity limit [49].

In summary, the presence of Au did not exhibit any influence on the crystalline planes such as of (111), (200), (220), and (311) that belong to CeO_2 or the crystal structure of the respective support except a negligible change in surface area.

3.3. Influence of Oxidation State of Au. Many studies [34, 38, 39, 51] emphasized the relationship between oxidation state of Au and catalytic activity of Au-catalysts. Mainly, the importance of oxidized Au was discussed; however, the nature of the oxidized Au was not well clarified except some recent studies [40, 41] claiming that Au^{+1} is the most active Au oxidation during the oxidation reaction. However, our results indicated that both Au^{+1} and Au^{+3} types of the Au are playing very important role for the high catalytic activity of the Au-catalysts.

Figure 5 provides a comparison of the deconvoluted Au 4f XPS spectra of all the prepared Au-catalysts. The oxidation states of the Au for each of the prepared Au-catalysts are summarized in Table 3. From the obtained data, it can be seen that, for $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst and $\text{Au}_{\text{HAuCl}_4}$ -Ce-Zr catalyst, both of Au^{+1} and Au^{+3} were present. Additionally, both of these catalysts had higher catalytic activity among the all studied Au-catalysts. In case of $\text{Au}_{\text{HAuCl}_4}$ -Zr catalyst and Au_{AuI} -Ce catalyst, only Au^{+1} was observed, and each of these catalysts has lower catalytic activity compared to that

FIGURE 4: Summary of the proposed reaction mechanism for the $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst.

of $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst. For the $\text{Au}_{\text{AuBr}_3}$ -Ce catalyst, which depicted the least catalytic activity, both Au^{+3} and quite high amount of negatively charged ionic Au Au^{-1} were observed.

Results indicate that presence of both Au^{+1} and Au^{+3} plays key role in the enhanced catalytic activity of the $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst as to that of Au^{+1} alone. The results also suggested that presence of Au^{-1} is not favorable for the activity of Au-catalyst. Based on the obtained results and current study, it is most probably that both Au^{+1} and Au^{+3} attack the C-H and C-C bond of the model compound, respectively, as the bond energy of C-H (413 KJ/mole) is higher as to that of C-C (347 KJ/mole). Thereon initiating a disturbance in the electronic cloud vicinity of the C-H and C-C bond ended with the formation of unstable radicals that can easily be attacked by the free electron present on or near the surface of reduced cerium oxide as shown in Figure 4.

3.4. TPR Studies. Solsona et al. [1] suggested that redox property of the catalyst is an important factor that may influence the catalytic activity of the catalysts for propane oxidation. Obtained TPR results indicated a strong relationship between reducibility and catalytic activity of the Au-catalysts. The TPR profiles of the catalysts are presented in Figure 6.

In case of CeO_2 , TPR peak was obtained at 517.3°C . Based on the literature, TPR profile of CeO_2 contains two major peaks, one at lower temperature (around 500°C), attributed to the reduction of oxygen on the surface, and one at higher temperature (around 800°C), related to the removal of bulk oxygen from the ceria structure [17, 52, 53]. Clearly, obtained result is consistent with the results in the literature.

The TPR peak of ZrO_2 , attributed to the reduction of oxygen on the surface [52], catalyst was obtained at 625.2°C . Idakiev et al. have also obtained the similar results [54].

The TPR peak of the support $\text{CeO}_2 + \text{ZrO}_2$ was obtained at 552.8°C . This peak represents the reduction of oxygen on the surface.

In short, the reducibility temperatures of the supports were in the order of $\text{CeO}_2 > \text{CeO}_2 + \text{ZrO}_2 > \text{ZrO}_2$, exactly in same order as to that of the catalytic activity of these supports.

The deposition of Au caused a strong effect on the reducibility of catalysts. Not only oxygen species possibly

FIGURE 5: Deconvoluted XPS spectra of the Au 4f in $\text{Au}_{\text{H2AuCl4}}$ -Ce catalyst, Au_{AuBr3} -Ce catalyst, Au_{AuI} -Ce catalyst, $\text{Au}_{\text{H2AuCl4}}$ -Zr catalyst, and $\text{Au}_{\text{H2AuCl4}}$ -Ce-Zr catalyst.

FIGURE 6: TPR study of $\text{Au}_{\text{H2AuCl4}}$ -Ce catalyst, $\text{Au}_{\text{H2AuCl4}}$ -Zr catalyst, and $\text{Au}_{\text{H2AuCl4}}$ -Ce-Zr catalyst, and corresponding supports.

adsorbed on Au nanoparticles were easily reducible, but also oxygen on the surface of catalysts was reduced at lower temperature than corresponding support. There were two TPR peaks for the $\text{Au}_{\text{H2AuCl4}}$ -Ce catalyst, the first peak is at

95°C, which attributes to the reduction of oxygen species near small Au nanoparticles, and the second peak is at 351°C, which attributes to reduction of oxygen on the surface [52].

There were also two TPR peaks for $\text{Au}_{\text{H2AuCl4}}$ -Zr catalyst, but they are registered at much higher temperature of 325°C and 515°C. These peaks might be attributed to the reduction of oxygen species near small Au nanoparticles and reduction of oxygen on the support surface, respectively. TPR profile for $\text{Au}_{\text{H2AuCl4}}$ -Ce-Zr catalyst was found to be similar to that for $\text{Au}_{\text{H2AuCl4}}$ -Ce catalyst. However, compared to the $\text{Au}_{\text{H2AuCl4}}$ -Ce-Zr catalyst, the temperature for the first TPR peak was lower in case of Au-Ce catalyst. Additionally broader TPR peak was obtained for $\text{Au}_{\text{H2AuCl4}}$ -Ce catalyst than $\text{Au}_{\text{H2AuCl4}}$ -Ce-Zr catalyst.

The TPR result showed that redox property of the catalysts is one of the most important factors to influence catalytic activity of the catalysts for propane oxidation.

3.5. Influence of Particle Size of Au. Au particle size is considered to be the most critical factor, which is defining catalytic activity of gold in oxidation reactions [55–58]. It is widely accepted that the optimum Au particle size could be between 3 and 10 nm [29, 58–60].

FIGURE 7: STEM images of $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst (a), $\text{Au}_{\text{AuBr}_3}$ -Ce catalyst (b), and Au_{AuI_3} -Ce catalyst (c).

It is well known that the fraction of surface Au atoms increases with the decrease in Au particle size and ultimately leads to the increased mobility of surface Au atoms. Additionally, the overlap of electron orbitals is lesser, as the average number of bonds between atoms becomes less. This leads to the band structure weakening, due to which surface atoms, in particular, start behaving as individuals rather than being in association with other atoms. This ultimately results in a greater fraction of the atoms in contact with the support [61].

Generally Au particle size depends on the nature of the support, preparation method, pH, calcination temperature, and precipitating agent [21–24, 36, 62–64]. Interestingly, they are the same parameters affecting catalytic activity of the Au-catalysts.

In order to study the effect of different precursor to Au particle size, STEM measurement was carried out for the gold catalysts prepared by using three different gold precursors (as shown in Figure 7). The average Au particle size for each catalyst obtained by STEM is summarized in Table 3. The results showed that, in case of $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst, Au

particles are uniformly dispersed on the support, with an average Au particle size of around 5 nm. However, in case of the other two catalysts $\text{Au}_{\text{AuBr}_3}$ -Ce and Au_{AuI_3} -Ce, Au has aggregated into large size of particles and average Au particle sizes for these two catalysts were found to be almost three times larger than that of $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst. This could explain why these two catalysts have shown less catalytic activity as to that of $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst.

4. Conclusions

Gold precursors strongly affect the size and dispersion of nano-Au within the Au-catalysts. Because of high dispersion and smaller size of Au particles, $\text{Au}_{\text{HAuCl}_4}$ -Ce catalyst showed the highest catalytic activity for propane oxidation. Based on obtained results, the nature of both Au precursor and support strongly influences catalytic activity of the Au-catalysts for the complete propane oxidation. CeO_2 has shown to be the best catalytic support. It showed the highest catalytic activity in comparison to the other studied supports.

The Au-catalyst obtained by using CeO_2 as support has shown the highest catalytic activity. The $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ Au precursor is the most suitable and effective precursor for preparation of highly active Au-catalyst. The use of other two Au precursors AuI and/or AuBr_3 leads to preparation of the catalysts of low catalytic activity. Surface properties of the catalysts exhibited that support having large surface area and small crystallites size is favorable for the preparation of highly catalytically active Au-catalyst. XPS study showed that presence of both Au^{+3} and Au^{+1} oxidation states is playing a key role for the enhanced catalytic activity of the Au-catalyst for the complete propane oxidation. Deposition of Au on the support significantly improves the redox ability of the support that ultimately leads to the enhanced catalytic activity. STEM result showed that nano-Au particle size is mandatory for high catalytic activity of the catalyst, and nature Au precursors strongly affect the size and dispersion of Au nanoparticles.

Nature of both Au precursor and support and oxidation state, surface properties, size, and dispersion of the Au particle are key parameters for obtaining highly active Au-catalysts.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors would like to acknowledge the King Abdulaziz University, Jeddah, for funding this project under Grant D-005/431. The authors would also like to acknowledge Raouf Ahmad and Florencio Trovela for all their technical support and assistance.

References

- [1] B. E. Solsona, T. Garcia, C. Jones, S. H. Taylor, A. F. Carley, and G. J. Hutchings, "Supported gold catalysts for the total oxidation of alkanes and carbon monoxide," *Applied Catalysis A: General*, vol. 312, no. 1-2, pp. 67-76, 2006.
- [2] L. Delannoy, K. Fajerwerg, P. Lakshmanan, C. Potvin, C. Méthivier, and C. Louis, "Supported gold catalysts for the decomposition of VOC: total oxidation of propene in low concentration as model reaction," *Applied Catalysis B: Environmental*, vol. 94, no. 1-2, pp. 117-124, 2010.
- [3] M. Lamalle, H. E. Ayadi, C. Gennequin et al., "Effect of the preparation method on Au/Ce-Ti-O catalysts activity for VOCs oxidation," *Catalysis Today*, vol. 137, no. 2-4, pp. 367-372, 2008.
- [4] M. Amann and M. Lutz, "The revision of the air quality legislation in the European Union related to ground-level ozone," *Journal of Hazardous Materials*, vol. 78, no. 1-3, pp. 41-62, 2000.
- [5] R. Heinsohn and R. Kabel, *Sources and Control of Air Pollution*, Prentice Hall, 1999.
- [6] A. C. Lewis, N. Carslaw, P. J. Marriott et al., "A larger pool of ozone-forming carbon compounds in urban atmospheres," *Nature*, vol. 405, no. 6788, pp. 778-781, 2000.
- [7] R. M. Heck, R. J. Farrauto, and S. T. Gulati, *Catalytic Air Pollution Control: Commercial Technology*, John Wiley & Sons, 2012.
- [8] W. B. Li, W. B. Chu, M. Zhuang, and J. Hua, "Catalytic oxidation of toluene on Mn-containing mixed oxides prepared in reverse microemulsions," *Catalysis Today*, vol. 93-95, pp. 205-209, 2004.
- [9] W. Li, J. Wang, and H. Gong, "Catalytic combustion of VOCs on non-noble metal catalysts," *Catalysis Today*, vol. 148, no. 1-2, pp. 81-87, 2009.
- [10] T. Masui, H. Imadzu, N. Matsuyama, and N. Imanaka, "Total oxidation of toluene on $\text{Pt/CeO}_2\text{-ZrO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts prepared in the presence of polyvinyl pyrrolidone," *Journal of Hazardous Materials*, vol. 176, no. 1-3, pp. 1106-1109, 2010.
- [11] T. Barakat, J. C. Rooke, M. Franco et al., "Pd- and/or Au-loaded Nb- and V-doped macro-mesoporous TiO_2 supports as catalysts for the total oxidation of VOCs," *European Journal of Inorganic Chemistry*, vol. 2012, no. 16, pp. 2812-2818, 2012.
- [12] M. Hosseini, S. Siffert, R. Cousin, A. Aboukais, Z. Hadj-Sadok, and B.-L. Su, "Total oxidation of VOCs on Pd and/or Au supported on $\text{TiO}_2/\text{ZrO}_2$ followed by "operando" DRIFT," *Comptes Rendus Chimie*, vol. 12, no. 6-7, pp. 654-659, 2009.
- [13] M. Haruta, "Size- and support-dependency in the catalysis of gold," *Catalysis Today*, vol. 36, no. 1, pp. 153-166, 1997.
- [14] T. Takei, I. Okuda, K. K. Bando, T. Akita, and M. Haruta, "Gold clusters supported on $\text{La}(\text{OH})_3$ for CO oxidation at 193 K," *Chemical Physics Letters*, vol. 493, no. 4-6, pp. 207-211, 2010.
- [15] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, and B. Delmon, "Low-temperature oxidation of CO over gold supported on TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, and Co_3O_4 ," *Journal of Catalysis*, vol. 144, no. 1, pp. 175-192, 1993.
- [16] M. Haruta, H. Sano, and T. Kobayashi, "Method for manufacture of catalyst composite having gold or mixture of gold with catalytic metal oxide deposited on carrier," Google Patents, 1987.
- [17] S. A. C. Carabineiro, S. S. T. Bastos, J. J. M. Órfão, M. F. R. Pereira, J. J. Delgado, and J. L. Figueiredo, "Exotemplated ceria catalysts with gold for CO oxidation," *Applied Catalysis A: General*, vol. 381, no. 1-2, pp. 150-160, 2010.
- [18] D. Widmann, Y. Liu, F. Schüth, and R. J. Behm, "Support effects in the Au-catalyzed CO oxidation—correlation between activity, oxygen storage capacity, and support reducibility," *Journal of Catalysis*, vol. 276, no. 2, pp. 292-305, 2010.
- [19] D. Wang, Z. Hao, D. Cheng, X. Shi, and C. Hu, "Influence of pretreatment conditions on low-temperature CO oxidation over $\text{Au/MO}_x/\text{Al}_2\text{O}_3$ catalysts," *Journal of Molecular Catalysis A: Chemical*, vol. 2007, no. 1-2, pp. 229-238, 2003.
- [20] G. C. Bond and D. T. Thompson, "Catalysis by gold," *Catalysis Reviews: Science and Engineering*, vol. 41, no. 3-4, pp. 319-388, 1999.
- [21] G. R. Bamwenda, S. Tsubota, T. Nakamura, and M. Haruta, "The influence of the preparation methods on the catalytic activity of platinum and gold supported on TiO_2 for CO oxidation," *Catalysis Letters*, vol. 44, no. 1-2, pp. 83-87, 1997.
- [22] S.-J. Lee and A. Gavrilidis, "Supported Au catalysts for low-temperature CO oxidation prepared by impregnation," *Journal of Catalysis*, vol. 206, no. 2, pp. 305-313, 2002.
- [23] R. Meyer, C. Lemire, S. K. Shaikhutdinov, and H.-J. Freund, "Surface chemistry of catalysis by gold," *Gold Bulletin*, vol. 37, no. 1-2, pp. 72-124, 2004.
- [24] H. H. Kung, M. C. Kung, and C. K. Costello, "Supported Au catalysts for low temperature CO oxidation," *Journal of Catalysis*, vol. 216, no. 1-2, pp. 425-432, 2003.

- [25] F. Moreau, G. C. Bond, and A. O. Taylor, "Gold on titania catalysts for the oxidation of carbon monoxide: Control of pH during preparation with various gold contents," *Journal of Catalysis*, vol. 231, no. 1, pp. 105–114, 2005.
- [26] A. Wolf and F. Schüth, "A systematic study of the synthesis conditions for the preparation of highly active gold catalysts," *Applied Catalysis A: General*, vol. 226, no. 1–2, pp. 1–13, 2002.
- [27] G. C. Bond, C. Louis, and D. T. Thompson, *Catalysis by Gold*, Imperial College Press, 2006.
- [28] M. A. P. Dekkers, M. J. Lippits, and B. E. Nieuwenhuys, "CO adsorption and oxidation on Au/TiO₂," *Catalysis Letters*, vol. 56, no. 4, pp. 195–197, 1998.
- [29] R. Zanella, S. Giorgio, C.-H. Shin, C. R. Henry, and C. Louis, "Characterization and reactivity in CO oxidation of gold nanoparticles supported on TiO₂ prepared by deposition-precipitation with NaOH and urea," *Journal of Catalysis*, vol. 222, no. 2, pp. 357–367, 2004.
- [30] V. R. Choudhary, V. P. Patil, P. Jana, and B. S. Uphade, "Nano-gold supported on Fe₂O₃: a highly active catalyst for low temperature oxidative destruction of methane green house gas from exhaust/waste gases," *Applied Catalysis A: General*, vol. 350, no. 2, pp. 186–190, 2008.
- [31] F. Boccuzzi, A. Chiorino, M. Manzoli et al., "Au/TiO₂ nanosized samples: a catalytic, TEM, and FTIR study of the effect of calcination temperature on the CO oxidation," *Journal of Catalysis*, vol. 202, no. 2, pp. 256–267, 2001.
- [32] M. Daté, Y. Ichihashi, T. Yamashita, A. Chiorino, F. Boccuzzi, and M. Haruta, "Performance of Au/TiO₂ catalyst under ambient conditions," *Catalysis Today*, vol. 72, no. 1–2, pp. 89–94, 2002.
- [33] V. I. Sobolev and L. V. Pirutko, "Room temperature reduction of N₂O by CO over Au/TiO₂," *Catalysis Communications*, vol. 18, pp. 147–150, 2012.
- [34] V. R. Choudhary, D. K. Dumbre, N. S. Patil, B. S. Uphade, and S. K. Bhargava, "Epoxidation of styrene by t-butyl hydroperoxide over gold nanoparticles supported on Yb₂O₃: effect of gold deposition method, gold loading, and calcination temperature of the catalyst on its surface properties and catalytic performance," *Journal of Catalysis*, vol. 300, pp. 217–224, 2013.
- [35] M. Olea, M. Tada, and Y. Iwasawa, "TAP study on carbon monoxide oxidation over supported gold catalysts Au/Ti(OH)₄* and Au/Fe(OH)₃*: moisture effect," *Journal of Catalysis*, vol. 248, no. 1, pp. 60–67, 2007.
- [36] H. S. Oh, J. Yang, C. Costello et al., "Selective catalytic oxidation of CO: effect of chloride on supported Au catalysts," *Journal of Catalysis*, vol. 210, no. 2, pp. 375–386, 2002.
- [37] S. A. Kondrat, G. Shaw, S. J. Freakley et al., "Physical mixing of metal acetates: a simple, scalable method to produce active chloride free bimetallic catalysts," *Chemical Science*, vol. 3, no. 10, pp. 2965–2971, 2012.
- [38] K. M. Parida, N. Sahu, P. Mohapatra, and M. S. Scurrall, "Low temperature CO oxidation over gold supported mesoporous Fe-TiO₂," *Journal of Molecular Catalysis A: Chemical*, vol. 319, no. 1–2, pp. 92–97, 2010.
- [39] H. Wang, H. Zhu, Z. Qin, F. Liang, G. Wang, and J. Wang, "Deactivation of a Au/CeO₂-Co₃O₄ catalyst during CO preferential oxidation in H₂-rich stream," *Journal of Catalysis*, vol. 264, no. 2, pp. 154–162, 2009.
- [40] E. Smolentseva, A. Simakov, S. Beloshapkin et al., "Gold catalysts supported on nanostructured Ce-Al-O mixed oxides prepared by organic sol-gel," *Applied Catalysis B: Environmental*, vol. 115–116, pp. 117–128, 2012.
- [41] M. Sanchez-Dominguez, L. F. Liotta, G. Di Carlo et al., "Synthesis of CeO₂, ZrO₂, Ce_{0.5}Zr_{0.5}O₂, and TiO₂ nanoparticles by a novel oil-in-water microemulsion reaction method and their use as catalyst support for CO oxidation," *Catalysis Today*, vol. 158, no. 1–2, pp. 35–43, 2010.
- [42] J. Moore, C. Stanitski, and P. Jurs, *Principles of Chemistry: The Molecular Science*, Cengage Learning, Boston, Mass, USA, 2009.
- [43] A. C. Gluhoi, N. Bogdanchikova, and B. E. Nieuwenhuys, "The effect of different types of additives on the catalytic activity of Au/Al₂O₃ in propene total oxidation: transition metal oxides and ceria," *Journal of Catalysis*, vol. 229, no. 1, pp. 154–162, 2005.
- [44] B. Solsona, T. Garcia, E. Aylón et al., "Promoting the activity and selectivity of high surface area Ni-Ce-O mixed oxides by gold deposition for VOC catalytic combustion," *Chemical Engineering Journal*, vol. 175, no. 1, pp. 271–278, 2011.
- [45] S. Carrettin, P. Concepción, A. Corma, J. M. López Nieto, and V. F. Puentes, "Nanocrystalline CeO₂ increases the activity of Au for CO oxidation by two orders of magnitude," *Angewandte Chemie—International Edition*, vol. 43, no. 19, pp. 2538–2540, 2004.
- [46] H. Liu, A. I. Kozlov, A. P. Kozlova, T. Shido, K. Asakura, and Y. Iwasawa, "Active oxygen species and mechanism for low-temperature CO oxidation reaction on a TiO₂-supported Au catalyst prepared from Au(PPh₃)(NO₃) and as-precipitated titanium hydroxide," *Journal of Catalysis*, vol. 185, no. 2, pp. 252–264, 1999.
- [47] X. Zhang, H. Wang, and B.-Q. Xu, "Remarkable nanosize effect of zirconia in Au/ZrO₂ catalyst for CO oxidation," *The Journal of Physical Chemistry B*, vol. 109, no. 19, pp. 9678–9683, 2005.
- [48] M. Ousmane, L. F. Liotta, G. D. Carlo et al., "Supported Au catalysts for low-temperature abatement of propene and toluene, as model VOCs: support effect," *Applied Catalysis B: Environmental*, vol. 101, no. 3–4, pp. 629–637, 2011.
- [49] T. Sakwarathorn, A. Luengnaruemitchai, and S. Pongstabodee, "Preferential CO oxidation in H₂-rich stream over Au/CeO₂ catalysts prepared via modified deposition-precipitation," *Journal of Industrial and Engineering Chemistry*, vol. 17, no. 4, pp. 747–754, 2011.
- [50] X. Zhang, H. Shi, and B.-Q. Xu, "Comparative study of Au/ZrO₂ catalysts in CO oxidation and 1,3-butadiene hydrogenation," *Catalysis Today*, vol. 122, no. 3–4, pp. 330–337, 2007.
- [51] A. M. Ali, M. A. Daous, A. A. M. Khamis, H. Driss, R. Burch, and L. A. Petrov, "Strong synergism between gold and manganese in an Au-Mn/triple-oxide-support (TOS) oxidation catalyst," *Applied Catalysis A: General*, vol. 489, pp. 24–31, 2014.
- [52] T. Tabakova, G. Avgouropoulos, J. Papavasiliou et al., "CO-free hydrogen production over Au/CeO₂-Fe₂O₃ catalysts: part I. Impact of the support composition on the performance for the preferential CO oxidation reaction," *Applied Catalysis B: Environmental*, vol. 101, no. 3–4, pp. 256–265, 2011.
- [53] O. H. Laguna, F. Romero Sarria, M. A. Centeno, and J. A. Odriozola, "Gold supported on metal-doped ceria catalysts (M = Zr, Zn and Fe) for the preferential oxidation of CO (PROX)," *Journal of Catalysis*, vol. 276, no. 2, pp. 360–370, 2010.
- [54] V. Idakiev, L. Ilieva, D. Andreeva, J. L. Blin, L. Gigot, and B. L. Su, "Complete benzene oxidation over gold-vanadia catalysts supported on nanostructured mesoporous titania and zirconia," *Applied Catalysis A: General*, vol. 243, no. 1, pp. 25–39, 2003.
- [55] Y. Zhu, S. Chen, X. Lu, Z. Yang, X. Feng, and H. Wang, "Oxidation of carbon monoxide over a fibrous titania-supported gold catalyst," *Chinese Journal of Catalysis*, vol. 30, no. 5, pp. 421–425, 2009.

- [56] T. A. Zepeda, A. Martinez-Hernández, R. Guil-López, and B. Pawelec, "Preferential CO oxidation in excess of hydrogen over Au/HMS catalysts modified by Ce, Fe and Ti oxides," *Applied Catalysis B: Environmental*, vol. 100, no. 3-4, pp. 450–462, 2010.
- [57] S. Ivanova, V. Pitchon, Y. Zimmermann, and C. Petit, "Preparation of alumina supported gold catalysts: influence of washing procedures, mechanism of particles size growth," *Applied Catalysis A: General*, vol. 298, no. 1-2, pp. 57–64, 2006.
- [58] K. Morgan, R. Burch, M. Daous et al., "Application of halo-hydrocarbons for the re-dispersion of gold particles," *Catalysis Science and Technology*, vol. 4, no. 3, pp. 729–737, 2014.
- [59] R. Grisel, K.-J. Weststrate, A. Gluhoi, and B. E. Nieuwenhuys, "Catalysis by gold nanoparticles," *Gold Bulletin*, vol. 35, no. 2, pp. 39–45, 2002.
- [60] M. Valden, X. Lai, and D. W. Goodman, "Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties," *Science*, vol. 281, no. 5383, pp. 1647–1650, 1998.
- [61] G. C. Bond, "Gold: a relatively new catalyst," *Catalysis Today*, vol. 72, no. 1-2, pp. 5–9, 2002.
- [62] S. Tsubota, T. Nakamura, K. Tanaka, and M. Haruta, "Effect of calcination temperature on the catalytic activity of Au colloids mechanically mixed with TiO₂ powder for CO oxidation," *Catalysis Letters*, vol. 56, no. 3-4, pp. 131–135, 1998.
- [63] M. Á. Centeno, I. Carrizosa, and J. A. Odriozola, "Deposition-precipitation method to obtain supported gold catalysts: Dependence of the acid-base properties of the support exemplified in the system TiO₂-TiOxNy-TiN," *Applied Catalysis A: General*, vol. 246, no. 2, pp. 365–372, 2003.
- [64] M. A. Centeno, K. Hadjiivanov, T. Venkov, H. Klimev, and J. A. Odriozola, "Comparative study of Au/Al₂O₃ and Au/CeO₂-Al₂O₃ catalysts," *Journal of Molecular Catalysis A: Chemical*, vol. 252, no. 1-2, pp. 142–149, 2006.