Research Article

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

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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_{HAuCl_4}-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 $Au(PPh_3)(NO)_3$ 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$_{HAuCl_4}$-Ce
1% Au-ZrO$_2$	Chloroauric acid trihydrate	Au$_{HAuCl_4}$-Zr
1% Au-75% CeO$_2$-25% ZrO$_2$	Chloroauric acid trihydrate	Au$_{HAuCl_4}$-Ce-Zr
1% Au-CeO$_2$	Gold (III) bromide	Au$_{AuBr_3}$-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 CeO$_2$ and ZrO$_2$ supports and different Au halogen containing precursors, such as HAuCl$_4$·3H$_2$O, AuBr$_3$, 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 (HNO$_3$) 69%, UN 2013; magnesium citrate (C$_{12}$H$_{10}$Mg$_3$O$_{14}$·9H$_2$O) 95%, Fluka; cerium oxide (CeO$_2$) 99.90%, Acros; zirconium oxide (ZrO$_2$) 99.90%, Aldrich; chloroauric acid (HAuCl$_4$) 99.95%, Acros; Au bromide (AuBr$_3$) 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, CeO$_2$ and ZrO$_2$, and double oxide mechanical mixture of 7.5 gms CeO$_2$ and 2.5 gm ZrO$_2$ 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 cm^3 of 0.1 M KOH and 3.86 cm^3 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 cm^3 DIW using different gold precursors (HAuCl$_4$·3H$_2$O, AuBr$_3$ 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 HNO$_3$. 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 AgNO$_3$ 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 CO$_2$ 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-cm^3 gas

sample, Agilent DB1/122-1063 (1 μm, 60 m × 0.25 mm) and HayeSep Q (2.4 m) columns, and He and N_2 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% H_2 in N_2 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-Kα, 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 Kα1 radiation was used to irradiate the sample with 30 KV and 30 mA. Routine spectra were recorded with 2θ (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_{HAuCl_4}-Ce, Au_{HAuCl_4}-Zr, and Au_{HAuCl_4}-Ce-Zr as well as for their supports CeO_2 and ZrO_2 and the CeO_2-ZrO_2 mixture.

All the supports have low catalytic activity. Under the same reaction conditions, the CeO_2 has shown the highest catalytic activity as compared to the other two, ZrO_2 and CeO_2-ZrO_2 samples. At 400°C, over CeO_2 around 40% of the propane was oxidized. While at same reaction temperature and GHSV, over the ZrO_2 propane conversion was less than 5%.

The catalytic activity of the CeO_2-ZrO_2 mixture was between activities of the CeO_2 and ZrO_2. At 400°C nearly
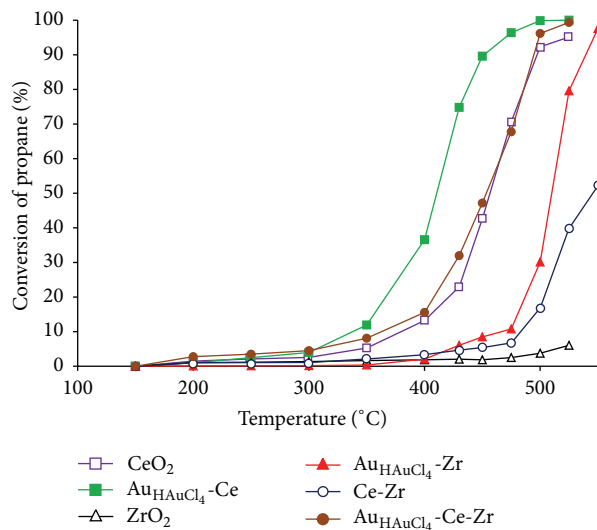

Figure 1: Comparison of the catalytic activity of the supports, Au_{HAuCl_4}-Ce catalyst, Au_{HAuCl_4}-Zr catalyst, and Au_{HAuCl_4}-Ce-Zr catalyst at GHSV 24000 h^{-1}.

10% of the propane was oxidized. However, the mixture of both ZrO_2 and CeO_2 had shown increased catalytic activity at temperatures above 400°C in comparison to ZrO_2 alone, which is because of the presence of CeO_2. Therefore, CeO_2, 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_{HAuCl_4}-Ce, Au_{HAuCl_4}-Zr, and Au_{HAuCl_4}-Ce-Zr were higher than the catalytic activities of the corresponding supports. Among the Au-catalysts, the Au_{HAuCl_4}-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_{HAuCl_4}-Ce-Zr and Au_{HAuCl_4}-Zr, the 50% conversions were achieved at higher temperatures of 450°C and 510°C, respectively. Au_{HAuCl_4}-Ce-Zr sample is more active than the Au_{HAuCl_4}-Zr, and the catalytic activity of Au_{HAuCl_4}-Ce-Zr is higher than catalytic activity of the Au_{HAuCl_4}-Zr. Difference between catalytic activity of Au_{HAuCl_4}-Zr and ZrO_2 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 CeO_2 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_{HAuCl_4}-Ce, Au_{AuBr_3}-Ce, and Au_{AuI}-Ce) prepared by using three different Au precursors HAuCl$_4$·3H$_2$O, AuBr$_3$, and AuI on the support CeO_2.

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_{HAuCl_4}-Ce	132.0	Fluorite cubic	~5 nm	23	
Au_{AuBr_3}-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_{HAuCl_4}-Zr	80.3	Amorphous	—		72
Ce-Zr	118.0	Fluorite cubic		24	24
Au_{HAuCl_4}-Ce-Zr	120.1	Fluorite cubic	—	20	26

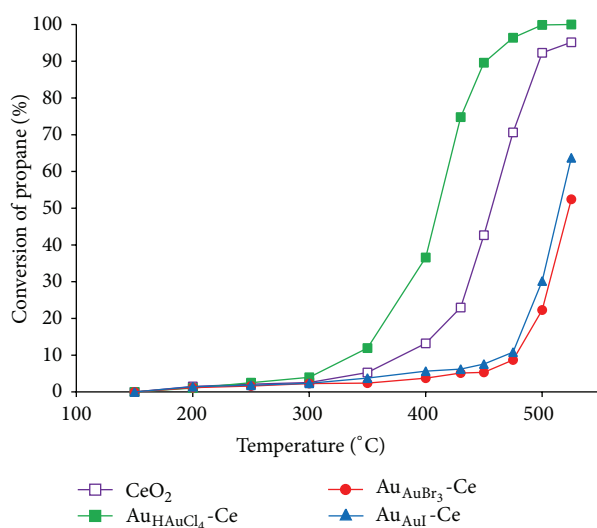[a]Obtained by N_2 adsorption; [b]obtained by XRD; [c]obtained by STEM.

FIGURE 2: Catalytic activity comparison of the Au_{HAuCl_4}-Ce catalyst, Au_{AuBr_3}-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_{HAuCl_4}-Ce catalyst has the highest catalytic activity (nearly 100% conversion at 450°C) in comparison to the other two catalysts Au_{AuBr_3}-Ce and AuI Au_{AuI}-Ce. The lowest catalytic activity was registered for Au_{AuBr_3}-Ce: 50% conversion of propane was achieved at 520°C. Catalytic performance of the Au_{AuI}-Ce was slightly better than that of Au_{AuBr_3}-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 $HAuCl_4 \cdot 3H_2O$ > 1.6×10^{-23} for AuI > 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_{HAuCl_4}-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, CeO_2 has the highest surface area and the most effective support to enhance catalytic activity of Au-catalysts, whereas ZrO_2 has shown least surface area and lowest catalytic activity among the supports. Surface area of CeO_2-ZrO_2 was found to be in between CeO_2 and ZrO_2, 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 CeO_2 and CeO_2-ZrO_2 and for corresponding Au-catalysts. In addition, smaller crystal size was observed for these catalysts (20~25 nm). While for ZrO_2 and Au_{HAuCl_4}-Zr catalyst, part of the ZrO_2 is amorphous and crystal size of the rest of the ZrO_2 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:

(i) 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 Au_{HAuCl_4}-Ce catalyst, Au_{AuBr_3}-Ce catalyst, Au_{AuI}-Ce catalyst, Au_{HAuCl_4}-Zr catalyst, and Au_{HAuCl_4}-Ce-Zr catalyst obtained by deconvolution of Au 4f peaks.

Catalyst	Gold oxidation state
Au_{HAuCl_4}-Ce	Au^{+1}, Au^{+3}
Au_{AuBr_3}-Ce	Au^{+3}, Au^-
Au_{AuI}-Ce	Au^{+1}
Au_{HAuCl_4}-Zr	Au^{+1}
Au_{HAuCl_4}-Ce-Zr	Au^{+1}, Au^{+3}
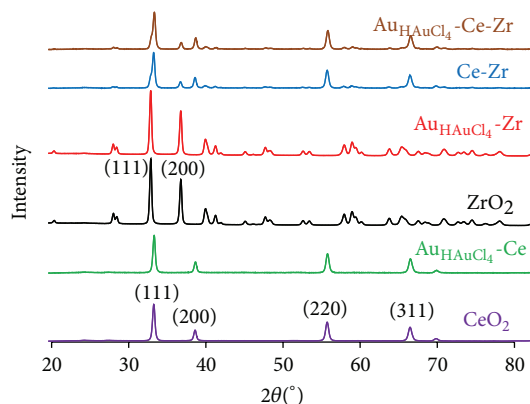
FIGURE 3: XRD pattern of the supports, Au_{HAuCl_4}-Ce catalyst, Au_{HAuCl_4}-Zr catalyst, and Au_{HAuCl_4}-Ce-Zr catalyst at GHSV 24000 h^{-1}.

    (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 Au_{HAuCl_4}-Ce catalyst and Au_{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 Au_{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
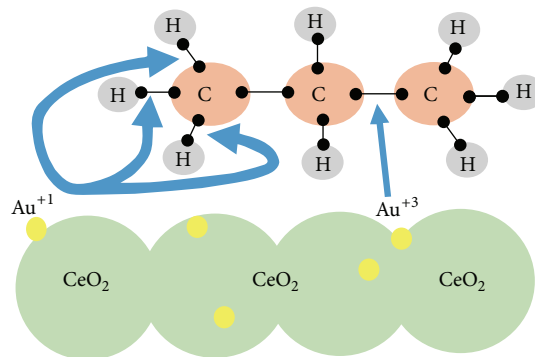

FIGURE 4: Summary of the proposed reaction mechanism for the Au_{HAuCl_4}-Ce catalyst.

of Au_{HAuCl_4}-Ce catalyst. For the Au_{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 Au_{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 $CeO_2 + ZrO_2$ 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 $CeO_2 > CeO_2 + ZrO_2 > ZrO_2$, 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
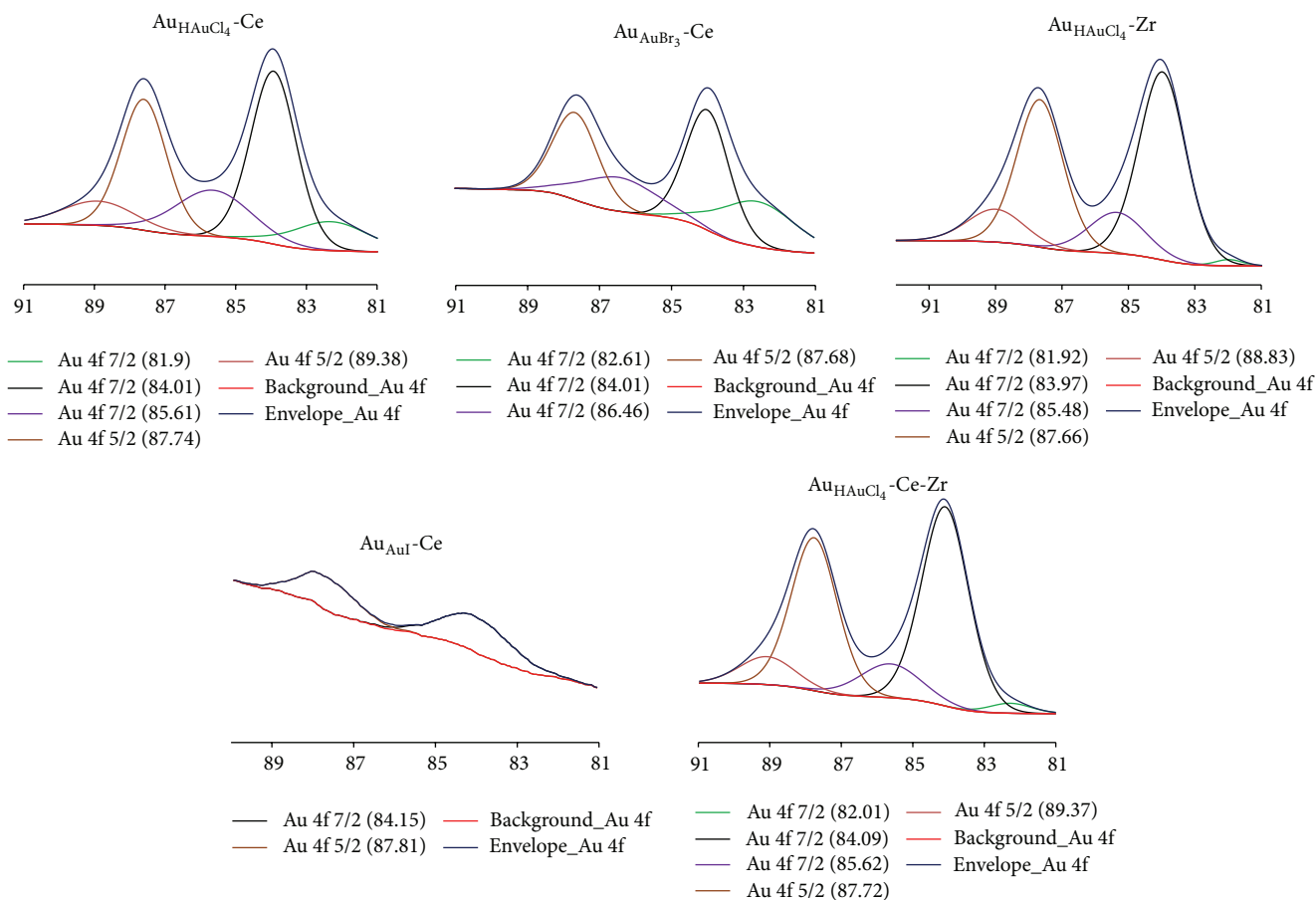
FIGURE 5: Deconvoluted XPS spectra of the Au 4f in Au_{HAuCl_4}-Ce catalyst, Au_{AuBr_3}-Ce catalyst, Au_{AuI}-Ce catalyst, Au_{HAuCl_4}-Zr catalyst, and Au_{HAuCl_4}-Ce-Zr catalyst.
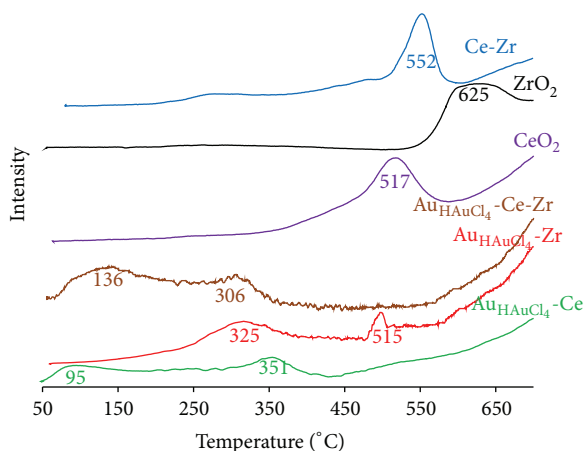

FIGURE 6: TPR study of Au_{HAuCl_4}-Ce catalyst, Au_{HAuCl_4}-Zr catalyst, and Au_{HAuCl_4}-Ce-Zr catalyst, and corresponding supports.

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 Au_{HAuCl_4}-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 Au_{HAuCl_4}-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 Au_{HAuCl_4}-Ce-Zr catalyst was found to be similar to that for Au_{HAuCl_4}-Ce catalyst. However, compared to the Au_{HAuCl_4}-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 Au_{HAuCl_4}-Ce catalyst than Au_{HAuCl_4}-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].
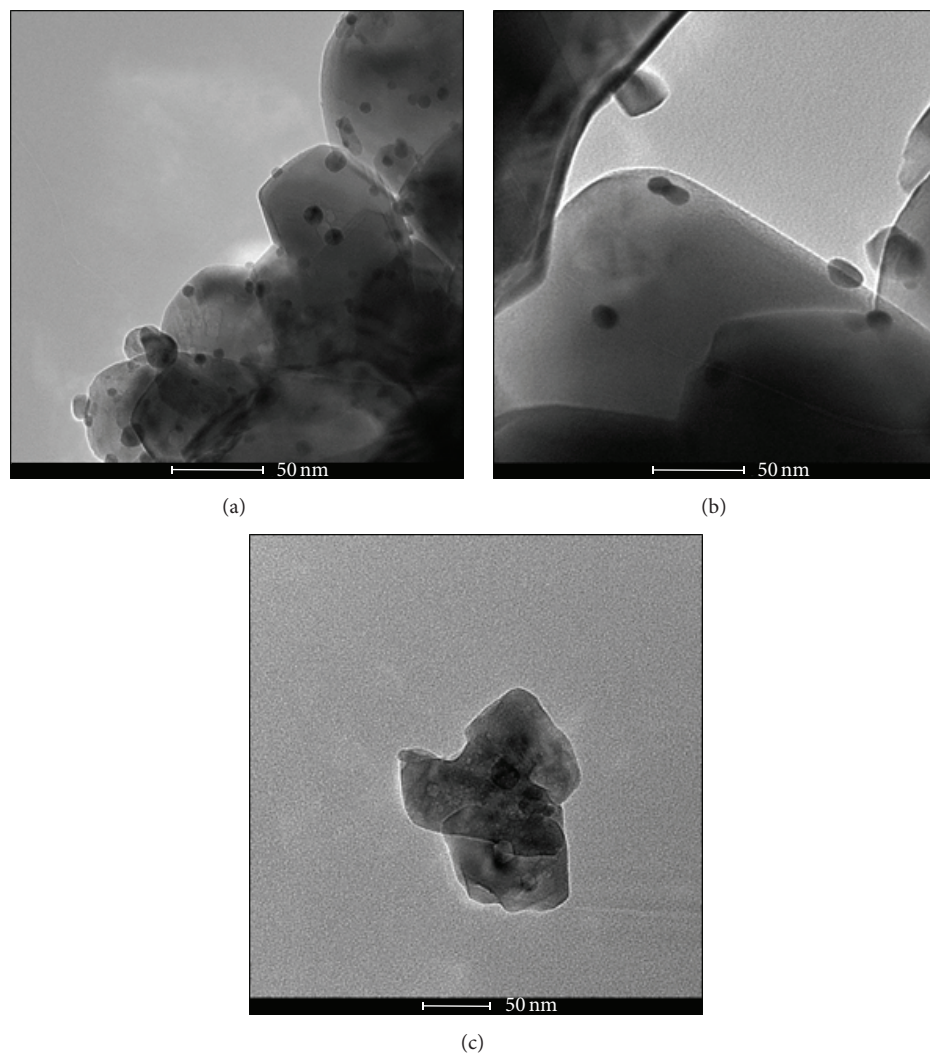
(a)

(b)

(c)

FIGURE 7: STEM images of Au_{HAuCl_4}-Ce catalyst (a), Au_{AuBr_3}-Ce catalyst (b), and Au_{AuI}-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 Au_{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 Au_{AuBr}-Ce and Au_{AuI}-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 Au_{HAuCl_4}-Ce catalyst. This could explain why these two catalysts have shown less catalytic activity as to that of Au_{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, Au_{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 $HAuCl_4 \cdot 3H_2O$ 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

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