

Ionic gold and catalytic activity of gold catalysts for CO oxidation

A. M. Ali

Department of Chemical and Materials Engineering, Faculty of Engineering, King Abdulaziz University
P.O. Box 80204, Jeddah 21589, Kingdom of Saudi Arabia

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This study is aimed to investigate the catalytic activity of freshly prepared gold catalysts supported on three metal oxide supports CeO₂, ZrO₂ and mechanically mixed CeO₂+ZrO₂ (DOS) for the CO oxidation under atmospheric pressure. The catalytic activity of both Au/CeO₂ and Au/DOS were nearly the same and far higher than that of an Au/ZrO₂ sample. The higher catalytic activity of both the Au/CeO₂ and Au/DOS catalysts is attributed to the presence of Au⁺¹ and Ce⁺⁴ ions as well as to enhanced CeO₂ oxygen mobility in the presence of ZrO₂.

Key words: gold catalyst, ionic gold, ceria, CO oxidation.

INTRODUCTION

Traditionally, gold was considered one of the most stable metals [1]. In 1987, Haruta *et.al* found that gold nanoparticles have high catalytic activity for the CO oxidation, and overturned the conventional paradigm about the gold [2,3]. Currently gold catalysts has become one of the most studied catalysts, due to their high activity in many oxidation reactions at low temperatures [4]. This allows reduction of energy costs in the industry and offers low-cost solutions of many global environmental issues [5–9]. Additionally, the gold catalysts exhibit unusual selectivity in many important reactions [10,11]. Further, it is also cost-effective to use the gold catalysts for the industries [4,12].

It has been widely accepted that the performance of the gold catalysts depend on the size distribution of the gold particles, gold-support interaction and on the electronic properties of both gold and support [1, 4, 13–18]. Also, many other parameters such as nature of the support [3,19–21], preparation method [1,22,23], calcination conditions [24–28], as well as the pH [29] and the precipitating agent [30, 31] have strong influence on the catalytic behavior of the gold catalysts.

CO oxidation is one of the most widely studied fields of application of the gold catalysts [32–36] because of many important applications for this reaction at low temperature, such as gas sensors [37], carbon monoxide laser [30] and air purification [38], etc. Among the catalyst supports, ceria is one of the most widely studied carriers for gold catalysts, due to its ability to maintain high Au

dispersion. In addition, stabilized cationic Au species on the CeO₂ surface, and ceria redox property to exchange the available oxygen are very useful to produce a strong promoting effect on gold oxidation state [39–42]. Further, the catalytic performance of Au/CeO₂ can be improved by several methods such as doping with other metals, nano-crystallisation and mixing with other metal oxides [39,40,43]. Among these, mixing ceria with other metal oxides is found to be beneficial for the enhanced catalytic activity of gold catalysts. For example, the catalytic performance of Au/CeO₂-Co₃O₄ in the CO oxidation has been reported to be much higher than that of Au/CeO₂ [44]. Zirconia is another interesting metal oxide to mix with CeO₂, because it can retard ceria degradation, improve the redox property of the latter, and preserve the oxygen defects in the metal oxide structure [45].

Based on available literature and as per author's best knowledge, none of the study results have been reported on the possible catalytic activity of gold catalysts supported on a mixture of two metal oxides (CeO₂ and ZrO₂) and/or their comparison to each metal oxide as support during CO oxidation.

Therefore, the aim of this study is to investigate the impact of support type and the possible role of ionic gold during CO oxidation on the gold catalyst.

EXPERIMENTAL

Catalyst preparation

Precisely calculated 10 g of each pure CeO₂ (Rhodia) and pure ZrO₂ (Rhodia) or 10 g DOS [CeO₂ : ZrO₂ = 3:1] were mechanically mixed in a Power Sonic instrument. Well-dried support at 120 °C was further used in a Mettler Toledo Labmax reactor for gold deposition. 13.5 cm³ of 0.1M KOH

* To whom all correspondence should be sent
E-mail: amsali@kau.edu.sa

and 3.86 cm³ of deionised water (DIW) for each gram of the support were added to the reactor. Under controlled temperature (60 °C) and pH of 8.5, HAuCl₄·3H₂O was used as the gold precursor. 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 to remove any chloride ions. Details on six different freshly prepared catalysts are enlisted Table 1.

Catalytic activity testing

The catalytic activity studies were performed in a PID Microactivity Reference reactor system. The CO oxidation was carried out in a 4-mm-ID quartz reactor charged with 0.5 g of catalyst at 12000 GHSV under different temperatures. Gaseous flow rates were controlled by Bronkhorst mass flow controllers. A ramping rate of 10 °C/min was used to increase the reaction temperature. The catalytic activity at a particular temperature was measured under steady state temperature regime throughout the catalytic experiment by applying PID Microactivity Reference software. The concentrations of both CO and CO₂ reaction products were monitored by employing an online Agilent 7890A gas chromatography instrument. A GC ChemStation[®] B.04.03 (54) was applied to analyse and process the reaction data obtained by using HayeSep Q (8 ft) columns and N₂ as carrier gas. In addition, all the catalysts were tested twice to check reproducibility under set parameters of the PID Microactivity reference reactor.

Catalyst characterisation

Catalyst surface area was measured by means of Quantachrome Nova 2000 under standard operating conditions (see Table 1).

The XPS method was applied to identify the possible oxidation states of each element by using multi-technique surface analysis system (SPECS GmbH, Germany). The sample was irradiated with 13.5 kV under electron take-off-angle perpendicular to the sample surface plane. The charge correction was performed by sing C1s line (284.6 eV). A

SPECS XR-50 with Mg-K α was used as an X-ray source.

XRD analysis was conducted by Equinox system Inel CPS 180 powder diffractometer. X-ray diffraction patterns were obtained from CoK α under 30 kV and 30 mA. Both COD and ICDD databases were used to identify existing phases.

RESULTS AND DISCUSSION

Catalytic activity results

The catalytic activity of three samples of CeO₂, ZrO₂, and DOS supports is shown in Fig. 1. Up to 175 °C, all the studied supports showed practically negligible catalytic activity. However, in the temperature range of 175 to 250 °C, the catalytic activity of both ceria and DOS started to increase, whereas the catalytic activity of zirconia did not show any significant change. Up to 250 °C, the CO conversions over both CeO₂ and DOS were ~7%, whereas, at temperatures up to 250 °C, the zirconia sample manifested only ~3% CO conversion. In the temperature range of 250–300 °C, the CO conversion over the three supports reached almost 85% and remained almost stable upon further temperature rise. In general, the catalytic activities of both ceria and DOS were almost the same and were higher than that of zirconia.

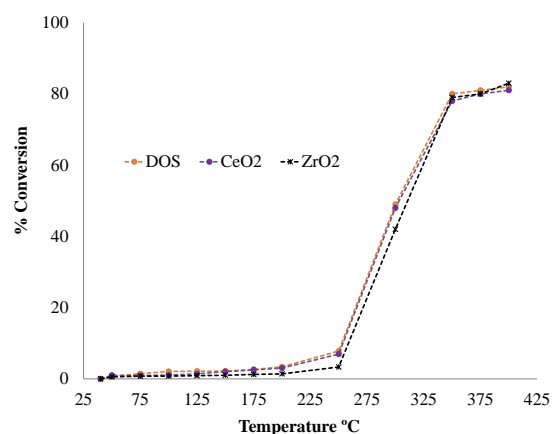


Fig. 1. Catalytic activity of the gold catalysts supports: DOS, CeO₂, and ZrO₂.

Table 1. Summary of the prepared catalysts

Catalyst Composition	Notation	Surface area (m ² g ⁻¹)	Gold particle size (nm)	Gold dominant oxidation state
100% CeO ₂	CeO ₂	131.1	-	-
100% ZrO ₂	ZrO ₂	80	-	-
75% CeO ₂ + 25% ZrO ₂	DOS	118.9	-	-
1% Au-CeO ₂	Au/CeO ₂	132	~ 5.1	Au ⁰ , Au ⁺¹
1% Au-ZrO ₂	Au/ZrO ₂	80.3	~ 4.5	Au ⁰ , Au ⁺¹
1% Au-CeO ₂ -ZrO ₂	Au/DOS	120.1	~ 4.0	Au ⁰ , Au ⁺¹ , Au ⁺³

CO conversions on three gold catalysts Au/DOS, Au/CeO₂, and Au/ZrO₂ are shown in Fig. 2. The gold catalysts are much more active in comparison with used metal oxide supports. In addition, catalyst carrier nature plays a crucial role to catalytic activity of the supported gold catalysts. In the case of Au/ZrO₂ catalyst, the conversion of CO was significantly increased. A maximum conversion was obtained above 150 °C. The Au/CeO₂ catalyst exhibited a much higher activity as to that of the Au/ZrO₂ catalyst.

The Au/DOS catalyst had almost similar catalytic activity with regard to the Au/CeO₂ catalyst. This is an indication that the addition of zirconia to the catalyst support slightly improves the catalytic activity of Au/DOS. In general, Au/DOS showed a maximum CO conversion at 150 °C.

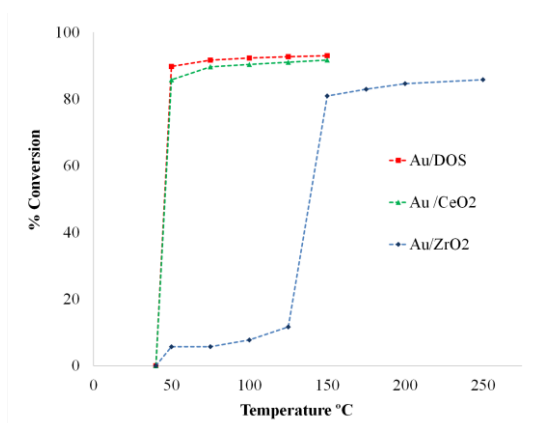


Fig. 2. Catalytic activity of the gold catalysts: Au/DOS, Au/CeO₂ and Au/ZrO₂.

XPS study

A detailed comparison of the overlay Au 4f XPS spectra of the Au/CeO₂, Au/ZrO₂, and Au/DOS catalysts is shown in Fig. 3. The binding energy

(BE) for metallic gold (Au⁰) is 84.0 eV. While the oxidized Au species Au⁺¹ have a BE of 85.5 eV, Au⁺³ shows a BE of 86.3 eV [46]. Metallic gold (Au⁰) and ionic gold (Au⁺¹) were the only species present in all the studied gold catalysts. The binding energy of the Au⁰/CeO₂ and Au⁰/DOS catalysts was found to be almost the same. Nevertheless, the binding energy of the Au/ZrO₂ catalyst was about 0.4 eV lower than that of the Au/CeO₂ and Au/DOS catalysts.

According to the literature [47], it is evident that the concentration of oxidized gold on the Au/ZrO₂ catalyst is lower as to that of the Au/CeO₂ and Au/DOS catalysts. Cerium is mainly present as Ce⁴⁺ in all the gold catalysts. It is well known that ceria can be partially reduced under X-ray radiation in the XPS instrument. However, the Ce³⁺ ions are formed also by influence of both gold species and zirconia. This result confirms that ceria can easily exchange oxygen with medium, and zirconia can improve the redox property of ceria, which play a key role in the CO oxidation.

XRD study

XRD analysis of all the gold catalysts (see Fig. 4) exhibited almost similar patterns as to that of support. It was found that after thermal treatment in the preparation procedure zirconia and ceria interact and form a mixed oxide Ce_{0.25}OZr_{0.75}O₄. The amount of the latter oxide is very small. This phase was registered after 24 h scanning of the sample. However, the addition of gold does not impart any significant changes to crystal structure. Therefore, only the Au oxidation states are the key reasons to enhance the catalytic activity of the studied gold catalyst.

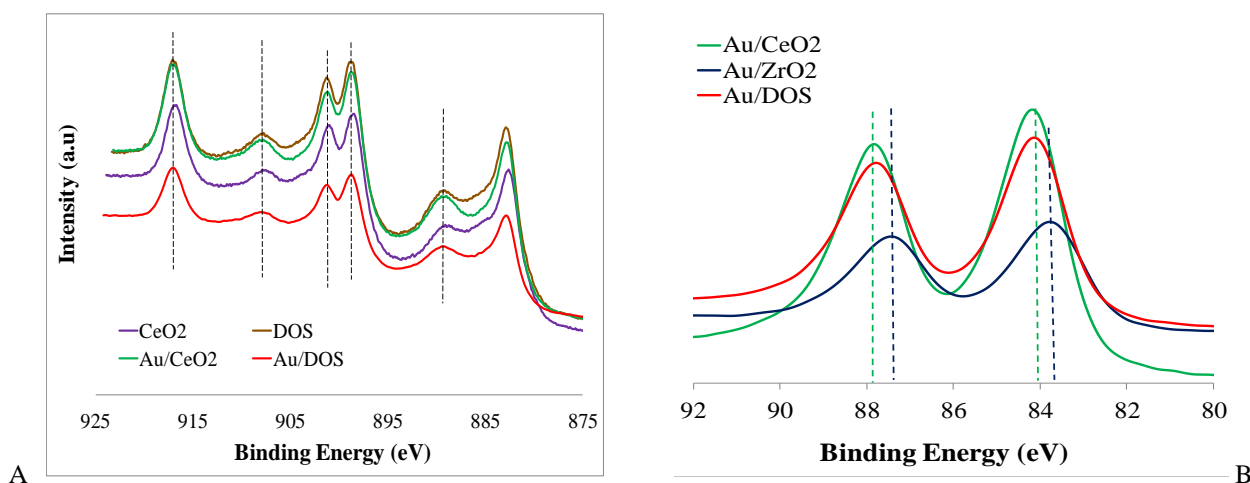


Fig. 3: Comparison of overlay XPS spectra: A - Ce 3d in CeO₂, DOS, Au/CeO₂, and Au/DOS catalysts; B - Au 4f for Au/DOS, Au/CeO₂, and Au/ZrO₂ catalysts.

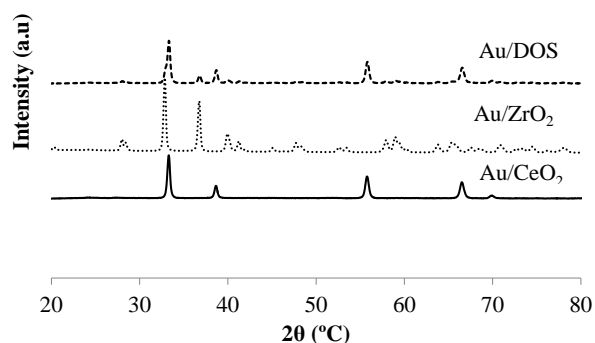


Fig. 4. XRD comparison of Au/DOS, Au/ZrO₂, and Au/CeO₂ catalysts.

CONCLUSIONS

All the studied gold catalysts showed a higher catalytic activity in comparison with applied support. Both the Au/CeO₂ and Au/DOS catalysts exhibited nearly the same catalytic activity for the CO oxidation at low temperature under atmospheric pressure, which was much higher than that of Au/ZrO₂. Under similar reaction conditions, the catalytic activity of the three supports (CeO₂, ZrO₂, and DOS) was nearly zero. The higher catalytic activity of both Au/CeO₂ and Au/DOS is because of the presence of ionic gold Au⁺¹ and Ce⁺⁴. Zirconia presence slightly improved ceria redox ability in the presence of gold. Further, this is helpful in promoting the oxidised gold species, which lead to enhanced catalytic activity.

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ЗЛАТНИ ЙОНИ И КАТАЛИТИЧНА АКТИВНОСТ НА ЗЛАТНИ КАТАЛИЗАТОРИ ЗА ОКИСЛЕНИЕ НА СО

А. М. Али

Департамент по инженерна химия и материали, Инженерен факултет, Университет „Крал Абдулазис“,
п.к. 80204, Джеда 21589, Кралство Саудитска Арабия

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(Резюме)

Изследвани са прясно приготвени златни катализатори нанесени върху три оксидни носителя CeO_2 , ZrO_2 и тяхна механична смес $\text{CeO}_2+\text{ZrO}_2$ (DOS) като катализатори за реакцията на окисление на СО при атмосферно налягане. Каталитичната активност на образци от Au/CeO_2 и Au/DOS е приблизително равна и е значително по-висока от активността на Au/ZrO_2 катализатор. Активността на изследваните златни катализатори се дължи на присъствието на златни Au^{+1} йони, на Ce^{+4} и на високата мобилност на кислорода в цериевия диоксид.