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Influence of the preparation method and silver content on the nature of active sites in Ag/CeO₂ catalysts used for propylene oxidation

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Abstract

Silver supported on ceria solids (1 and 4 wt% Ag) are prepared by three different methods: Impregnation–Reduction with Citrate (IRC), Deposition–Precipitation with Urea (DPU), and Wetness Impregnation (WI). The catalysts are tested in the total oxidation of propylene. Presence of Ag²⁺ with Ag⁺ improves the catalytic activity. The solid prepared by the (IRC) method with a silver loading of 4 wt%, shows a better catalytic activity compared to the other solids. H₂-Temperature Programmed Reduction (TPR) and Electron Paramagnetic Resonance (EPR) techniques confirm that the presence of three different redox couples: Ag²⁺/Ag⁺, Ag²⁺/Ag⁰, and Ag⁺/Ag⁰ in the (IRC) solid containing 4wt% of silver is responsible for its superior catalytic performance.

Keywords:

Ceria, Silver, Preparation method, EPR, TPR, Propylene total oxidation.

1. Introduction

Volatile organic compounds (VOC) are harmful pollutants. One promising way to eliminate diluted VOC is their total oxidation using catalysts. Silver based-catalysts are efficient solids among the catalytic systems studied in oxidation reactions. The catalytic activity and stability of such compounds depend on many criteria [1-10]: the silver particle

size, the presence of silver cations, the metal oxide support, the preparation method, the precursors used in these preparations, the calcination temperature and the pre-treatment procedure. Among these parameters, the preparation method has been reported to significantly affect the activity of the silver–cerium oxide system. The most common applied methods: impregnation, deposition–precipitation, and co-precipitation strongly influence the catalytic activity due to the large differences in silver particles size and/or to the availability of active silver sites in the vicinity of the support surface defects [7-10]. Previous studies [11-12] dealt with the preparation of silver supported catalysts by the deposition-precipitation (DP) or/and the impregnation (IM) methods and showed that DP leads to the formation of better performing catalysts in the oxidation reactions. This is attributed to the formation of silver nanoparticles in the catalysts prepared by DP compared to large silver particles obtained when using the IM method. In addition, Skaf et al. [4] obtained a better activity in propylene, CO, and soot oxidation over 10wt%Ag/CeO₂ (IM) compared to 10wt%Ag/CeO₂ (DP). This is assigned to an easier reduction of silver species and to the presence of Ag²⁺ species detected by electron paramagnetic resonance. In all the above mentioned studies [4, 11-12], a silver nitrate (AgNO₃) solution is used to introduce silver in the catalytic material.

Furthermore, cerium oxide (CeO₂) has received considerable attention especially in oxidation catalysis as catalyst or catalytic support [13-21]. This is due to its low temperature reducibility and its oxygen storage and release properties in the presence of noble or transition metal particles. The oxidation/reduction couple (Ce³⁺/Ce⁴⁺) of ceria particles which is in direct contact with the metal particles promotes the catalytic activity in most cerium based materials.

In this work, propylene is chosen as VOC model, CeO₂ as support, and silver species as active phase. Three different methods are used to synthesize the catalytic systems Ag/CeO₂: Impregnation–Reduction with Citrate (IRC), Deposition–Precipitation with Urea (DPU), and Wetness Impregnation (WI). Two different Ag loadings, 1 and 4 wt%, are studied. These two contents are chosen based on a previous study from our team [22] where different Ag contents ranging between 1 and 20 wt% were impregnated on ceria support, using silver nitrate as precursor, and evaluated in propylene total oxidation. The content 3.5wt% gave better activities than lower Ag contents and similar activities to higher Ag contents. In order not to make our catalysts expensive, we selected the content 4wt% and for the sake of comparison, we also prepared the content 1wt%. Ceria support used in this work being mesoporous, we expect higher dispersion of silver species over ceria support than in our previous work [22].

The performances of the systems prepared in this work are compared in total oxidation of propylene. The elucidation of the reasons for the differences in catalytic performances is then made, using the H₂-temperature programmed reduction (TPR) and the electron paramagnetic resonance (EPR) techniques.

2. Experimental part

2.1. Catalysts preparation

The catalysts are prepared by three different methods: impregnation–reduction with citrate (IRC), deposition–precipitation with urea (DPU), and wetness impregnation (WI). The detailed procedure of catalysts preparation, along with characterization of BET surface area and pore volume, are reported previously [7, 23]. The catalysts are calcined at 400°C. Besides pure ceria, CeO₂, the six prepared samples are designated by x%Ag/CeO₂(IRC) or (DPU) or (WI), where x is the silver loading in wt% (x = 1 or 4).

2.2. Catalytic tests

The catalysts are evaluated in the reaction of total oxidation of propylene. The experiments are carried out in a conventional fixed bed and plug-flow micro reactor, between 25 and 400°C (1°C.min⁻¹). The reactive mixture (100 mL min⁻¹) is composed of air and 6000 ppm of propylene. Before the catalytic test, the catalyst (200 mg) is pre-treated under a flow of air (2 L.h⁻¹) at 400°C (1°C.min⁻¹). The amounts of reactants and products are followed by a microgas phase chromatography equipped with thermo-conductivity detector (TCD) (Varian CP-4900 microGC). Propylene, C₃H₆, conversion is calculated as follows:

$$\text{C}_3\text{H}_6 \text{ conversion (\%)} = \frac{\% \text{ C}_3\text{H}_6 \text{ (initial)} - \% \text{ C}_3\text{H}_6 \text{ (remaining)}}{\% \text{ C}_3\text{H}_6 \text{ (initial)}} \times 100$$

Indeed, in our case the initial molar flow F of propylene as well as the catalyst weight m are kept constant. Therefore the ratio $\frac{F}{m}$ is constant and the rate " $r = \frac{F}{m} \times \text{conversion percentage}$ " is proportional to the conversion percentage and therefore the light-off curves reflect well the kinetic rate.

2.3. Characterization techniques

The Temperature Programmed Reduction (TPR) experiments are carried out in an Altamira AMI-200 apparatus. The TPR profiles are obtained by passing a 5% H₂/Ar flow (30 mL.min⁻¹) through 50 mg of samples heated at 5°C.min⁻¹ from ambient temperature to 900°C. The hydrogen concentration in the effluent is continuously monitored by a thermo-conductivity detector (TCD).

Electron Paramagnetic Resonance (EPR) measurements are performed at -196 °C and room temperature on an EMX BRUKER spectrometer with a cavity operating at a frequency of ~9.5 GHz (X band). 50 to 55 mg of the calcined catalysts are vacuum treated before analysis ($P = 1.2 \times 10^{-5}$ bar). The magnetic field is modulated at 100 kHz. The *g* values are determined from precise frequency and magnetic field values.

3. Results and discussions

3.1. Catalytic test

Figure 1 shows the propylene conversion as a function of reaction temperature on x%Ag/CeO₂ (IRC), (DPU), and (WI) catalysts. CO₂ and water are the only products detected during the reaction. Propylene conversion is enhanced when the silver content increases; 1%Ag/CeO₂ catalysts are less active than the corresponding 4%Ag/CeO₂ ones. Over the 1%Ag/CeO₂ catalysts, propylene conversion is not total even at 400°C. However, propylene conversion was complete in the presence of 4%Ag/CeO₂ catalysts at temperatures lower than 400°C. The temperature at which 50% of propylene is converted (*T*₅₀), is used to compare the catalytic performance. According to the results, the catalysts are ranked according to decreasing catalytic performance as follows : 4%Ag/CeO₂(IRC) > 4%Ag/CeO₂(WI) > 4%Ag/CeO₂(DPU) > 1%Ag/CeO₂(IRC) > 1%Ag/CeO₂(WI) > 1%Ag/CeO₂(DPU).

In order to explain the difference in the catalytic activities between the different studied samples, TPR and EPR characterization methods are used.

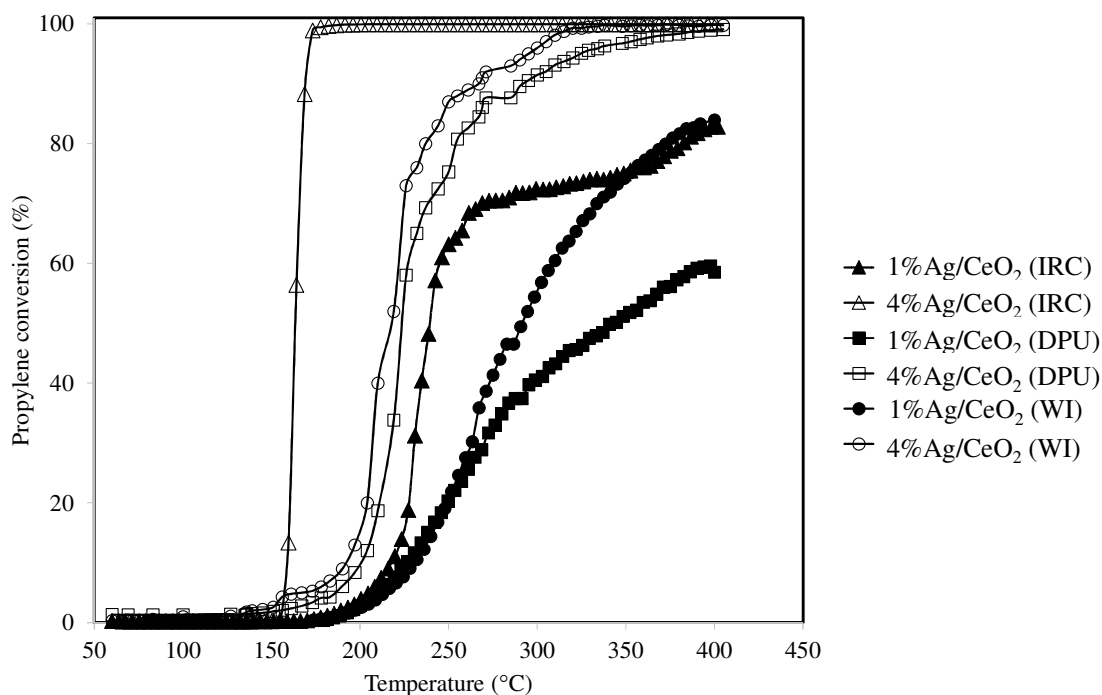


Figure 1: Propylene conversion versus reaction temperature on x%Ag/CeO₂ (IRC), (DPU), and (WI) catalysts, (x = 1 or 4 wt%).

3.2. TPR study

The TPR technique is used to study the surface and bulk reducibility of the catalysts. For pure ceria (Figure 2), two broad reduction peaks in the 300-550°C and the 600-850°C temperature ranges are observed. Similar results were already obtained in previous studies [15, 20-21]. The first peak is attributed to the reduction of ceria surface, with the formation of Ce³⁺ species and an oxygen lacuna. The second peak corresponds to the reduction of bulk ceria along with the reduction of Ce⁴⁺ into Ce³⁺ ions.

The TPR profiles of all x%Ag/CeO₂ catalysts are also shown in Figure 2. The surface ceria reduction peak shifted to lower temperatures in almost all catalysts. The position and shape of the first reduction peak depend on the silver content and preparation method. New reduction peaks are also observed at temperatures lower than 200°C on the TPR profiles of all silver containing catalysts.

For the 4%Ag/CeO₂(IRC) catalyst, two reductions peaks are observed at 81°C and 130°C while the peak corresponding to surface ceria was shifted to 340°C. For the 1%Ag/CeO₂(IRC)

catalyst, a reduction peak is observed at 128°C while surface and bulk ceria reductions yielded a broad and flattened peak.

For the 4%Ag/CeO₂(DPU) catalyst, a broad peak extending from 400°C to 750°C corresponds to surface and bulk ceria reduction. Two additional reduction peaks are present at 90°C and 179°C. The TPR profile of 1%Ag/CeO₂(DPU) presented one reduction peak at 167°C with no identified peak for surface ceria reduction.

The TPR profile of the 4%Ag/CeO₂(WI) catalyst is different as it shows that surface ceria reduction was delayed, peaking at 502°C, in addition to a new intense reduction peak observed at 173°C. For the 1%Ag/CeO₂ catalysts, ceria reduction peaks (surface and bulk) are barely observed in addition to a broad reduction peak centered at 103°C.

All reduction peaks observed at temperatures lower than 200°C can be attributed to the reduction of silver oxide species (Ag_xO_y). In literature, similar peaks were obtained at low temperatures for solids prepared by the impregnation and deposition-precipitation methods and were ascribed to the reduction of AgO and Ag₂O respectively [4, 24-25]. Peaks at temperatures lower than 100°C are ascribed to reduction of Ag²⁺ species (AgO into Ag₂O and Ag(0)) [4, 25]. Peaks at 100-180°C are attributed to the reduction of Ag₂O into Ag(0) [4, 24-25]. Reducibility of Ag⁺ species is easier when Ag⁺ species are in higher proximity or interaction with oxygen. For example, Ag⁺ species in 4% Ag/CeO₂(WI) show a maximum reduction at 173°C whereas in 1%Ag/CeO₂(IRC) this maximum is at 128°C, revealing that oxygen species are more close to Ag⁺ species in the latter [4].

Despite that the 4%Ag/CeO₂(IRC) catalyst contains species that reduce at the lowest observed temperatures, it cannot account for its superior catalytic performance. In fact, all catalysts with 4wt% of silver, showed reduction peaks at low and close temperature values (especially for temperatures lower than 100°C). The EPR technique is able to identify the nature of silver species present in the different catalysts and helps in the elucidation of the differences in catalytic performances.

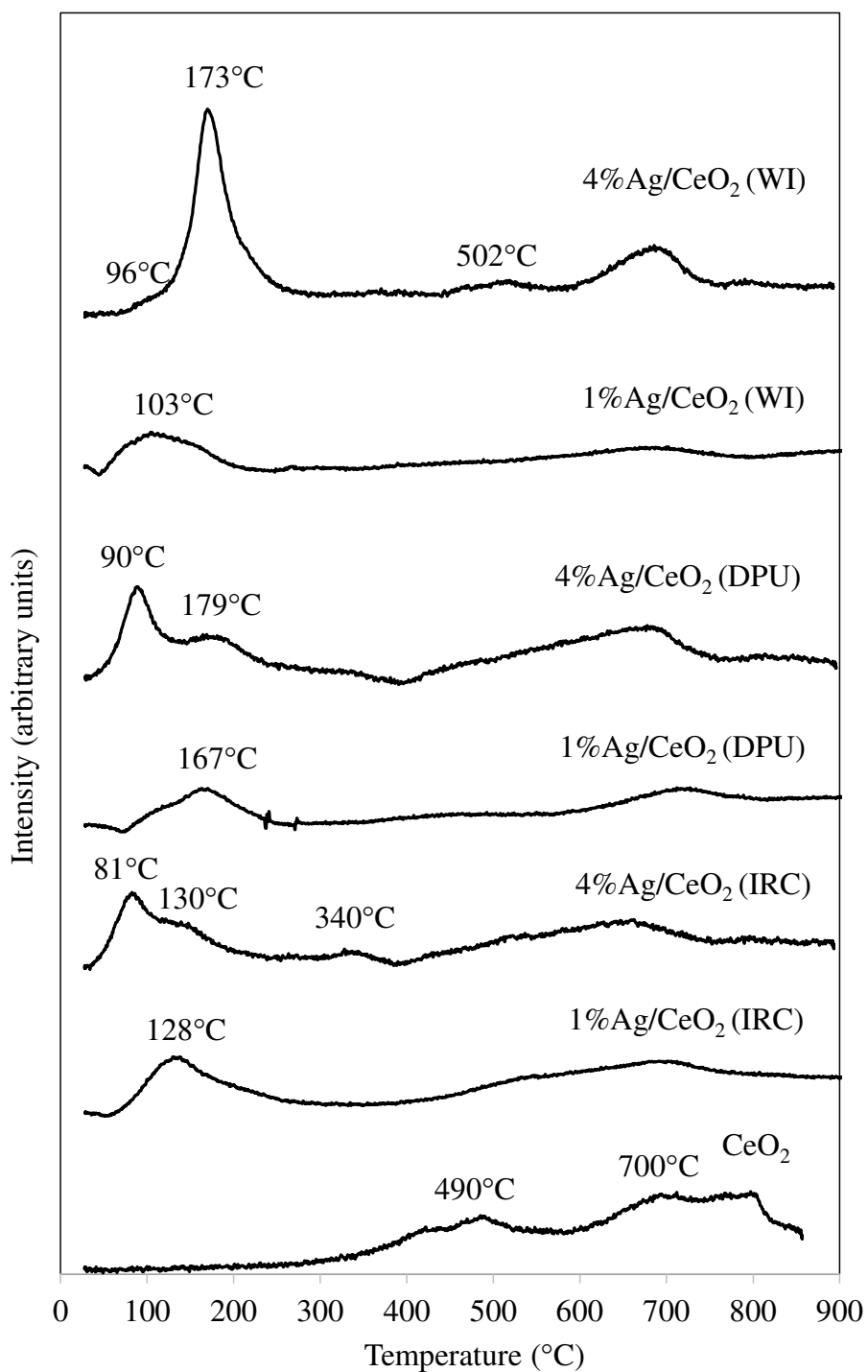


Figure 2: H₂-Temperature-programmed reduction (H₂-TPR) profiles of CeO₂ and x%Ag/CeO₂ (IRC), (DPU) and (WI) catalysts, (x = 1 or 4 wt%).

It is worthy to note that X-ray photoelectron (XPS) studies were performed on 10%Ag/CeO₂ prepared by impregnation (IM) and deposition-precipitation (DP) in a previous work from our

group [4]. Presence of Ag^+ (binding energies 367.7 and 374.2 eV), Ag^0 (binding energies 369.2 and 375.2 eV), and Ag^{2+} (binding energies 367.4 and 373.2 eV) was evidenced. Ag^{2+} was only evidenced in the IM sample and was behind the better catalytic performance of IM compared to DP in oxidation reactions of propylene, carbon black, and CO. It would be also interesting to perform XPS studies on our samples.

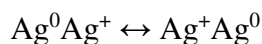
3.3. EPR study

Figure 3 shows the EPR spectra recorded at -196°C for the $x\%\text{Ag}/\text{CeO}_2$ catalysts (IRC, DPU, WI). Prior to analysis, the catalysts are calcined at 400°C for 4 h, and then treated under vacuum at the same temperature for 1 min.

The $1\%\text{Ag}/\text{CeO}_2(\text{IRC})$ spectrum (Figure 3.a) is composed of four signals. The first signal, denoted “C”, shows an orthorhombic symmetry with $g_{zz} = 1.980$, $g_{yy} = 1.964$, and $g_{xx} = 1.940$. This signal was extensively studied in the literature [26-29] and is attributed to Ce^{3+} ions. The second signal, denoted “S”, is an isotropic signal centred at $g = 2.0028$ with a peak-to-peak width; $\Delta H = 6$ G. It corresponds to a trapped electron in the ceria matrix [29-31]. The third signal, denoted “O”, has an axial symmetry with $g_{//} = 2.034$, $g_{\perp} = 2.011$, and is unambiguously attributed to O_2^- species located on Ce^{4+} ions. Indeed, a similar signal with a slight difference in the $g_{//}$ value is obtained after adsorption of molecular O_2 on pure ceria [32-34]. The “O” signal remains stable, and its intensity decreases according to the Curie law when the spectrum is recorded at room temperature (Figure 4a). This means that the O_2^- species is strongly adsorbed on ceria. Finally, the last signal, denoted “G”, is characterized by a doublet of lines centered at $g_{\perp} = 2.038$ with a hyperfine splitting constant of $A_{\perp} = 24$ G. This new signal can be attributed to Ag^{2+} ions despite the absence of their parallel components. Indeed, similar doublets were obtained on numerous solids containing silver [4-6]. Indeed, TPR peak ascribed to reduction of silver species in $1\%\text{Ag}/\text{CeO}_2(\text{IRC})$, with maximum at 128°C is broad. It starts at temperature lower than 100°C . Therefore it is not excluded the existence of some Ag^{2+} species with Ag^+ in this sample. As EPR is very sensitive, the presence of Ag^{2+} is well evidenced by this technique.

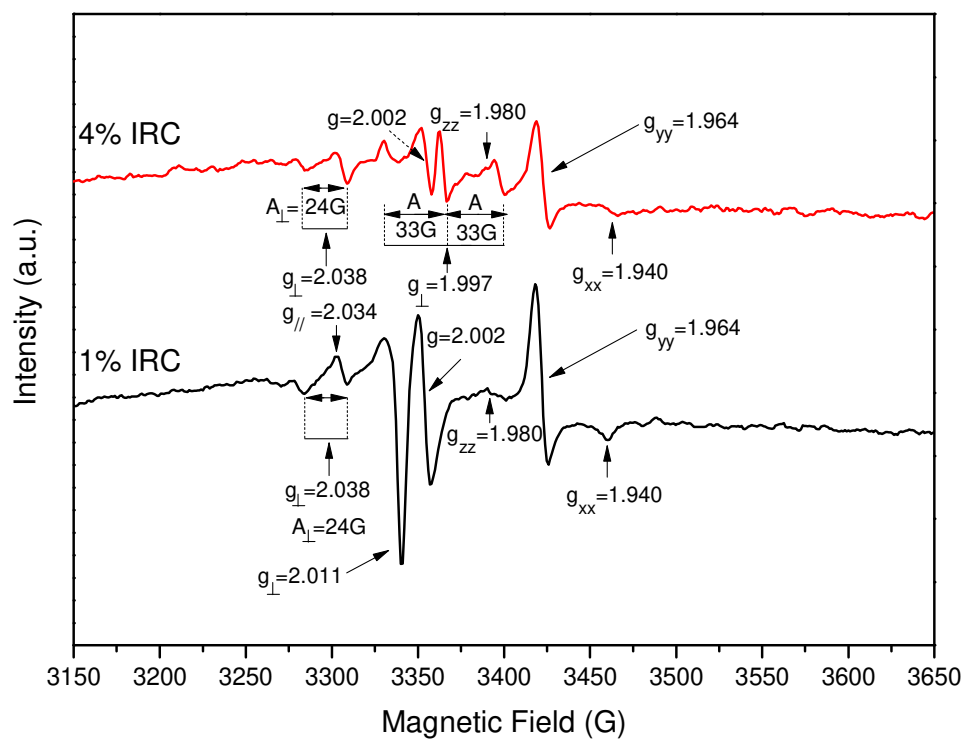
The $4\%\text{Ag}/\text{CeO}_2(\text{IRC})$ spectrum contains four signals. Three of these signals correspond to the already identified “C”, “S”, and “G” signals. These signals have different intensities compared to $1\%\text{Ag}/\text{CeO}_2(\text{IRC})$. However, the “O” signal is absent and a new signal, denoted

“T”, is present. The “T” signal consists of a triplet centered at $g = 1.997$ with a hyperfine splitting constant of 33 G. The intensities ratios of the three lines composing this triplet are 1:2:1. This triplet “T” can be unambiguously attributed to an unpaired electron shared between two equivalent entities possessing each a nuclear spin of $I=1/2$. These entities can be in the form of:

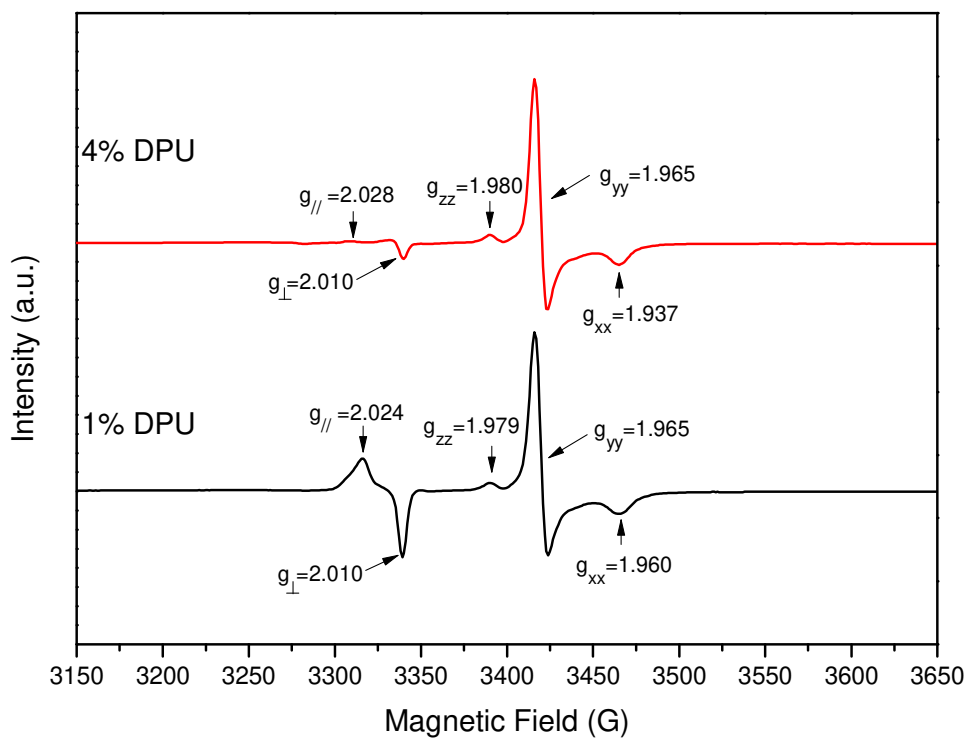


Despite the absence of the O_2^- species in the 4%Ag/CeO₂(IRC) catalyst, it contains Ag^{2+} , Ag^+ , and Ag^0 species which means that three different redox couples; $\text{Ag}^{2+}/\text{Ag}^+$, $\text{Ag}^{2+}/\text{Ag}^0$, and Ag^+/Ag^0 ; are available. The presence of these redox couples in the 4%Ag/CeO₂(IRC) catalyst accounts for its superior catalytic activity in the total oxidation of propylene compared to the 1%Ag/CeO₂(IRC) catalyst which only contains the $\text{Ag}^{2+}/\text{Ag}^+$ redox couple.

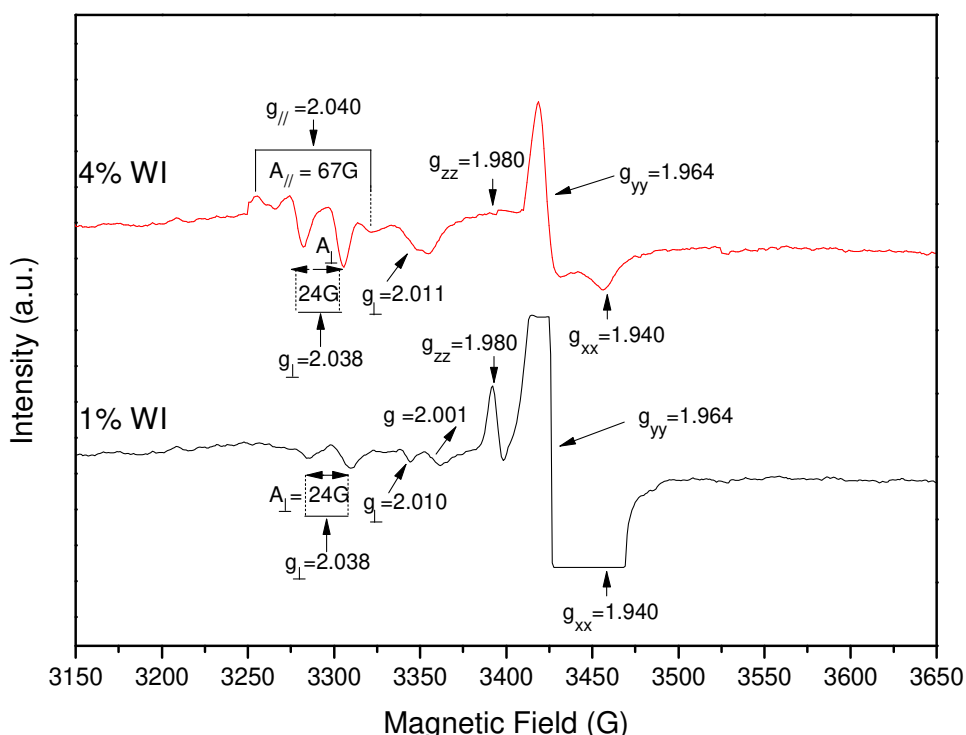
Figure 3.b shows the EPR spectra recorded at -196°C for the x%Ag/CeO₂(DPU) catalysts. The 1%Ag/CeO₂(DPU) spectrum contains two signals. The “C” signal discussed previously and a second signal, denoted “O” with an axial symmetry ($g_{\parallel} = 2.024$ and $g_{\perp} = 2.010$) attributed to O_2^- species located on ceria surface. The O_2^- species remained stable when the spectrum is recorded at room temperature (Figure 4.b). The EPR spectrum of 4%Ag/CeO₂(DPU) shows three signals. A “C” signal, an “O” signal ($g_{\parallel} = 2.028$ and $g_{\perp} = 2.009$) obtained at -196°C (Figure 3.b) and room temperature (Figure 4.b) corresponding to surface O_2^- species and a “G” signal centred at $g_{\perp} = 2.038$ with a hyperfine splitting constant equal to 24 G. This “G” signal is attributed to the presence of Ag^{2+} ions in the catalyst. The presence of these Ag^{2+} ions for high silver content is probably responsible for the superior catalytic activity of 4%Ag/CeO₂(DPU) compared to 1%Ag/CeO₂(DPU) in propylene oxidation [4].



3.a



3.b.

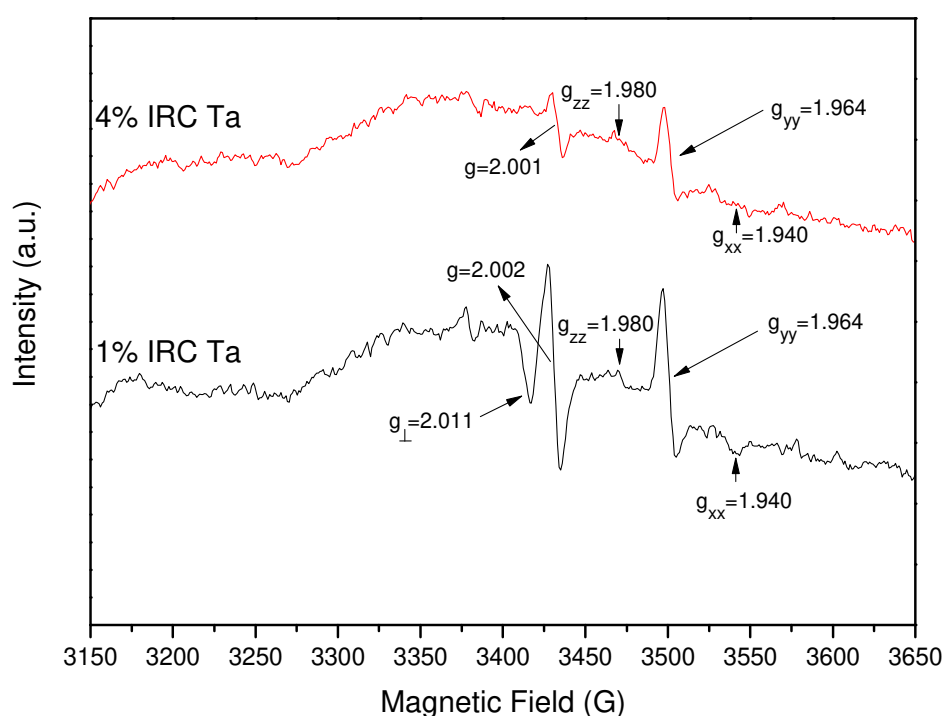


3.c.

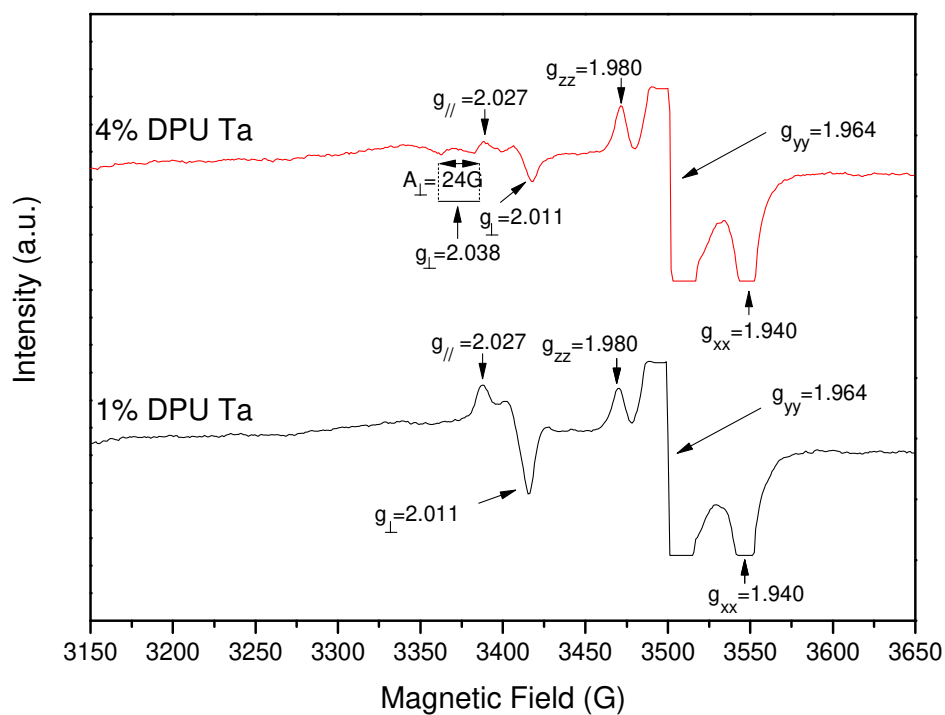
Figure 3: Electron paramagnetic resonance (EPR) spectra, recorded at -196°C , of $x\%\text{Ag}/\text{CeO}_2$ catalysts ($x = 1$ or 4 wt%), a) (IRC), b) (DPU) and c) (WI).

Figure 3.c presents the EPR spectra recorded at -196°C for the $x\%\text{Ag}/\text{CeO}_2(\text{WI})$ catalysts. The $1\%\text{Ag}/\text{CeO}_2(\text{WI})$ spectrum contains the four “C”, “S”, “O”, and “G” signals already observed for the EPR spectrum of the $1\%\text{Ag}/\text{CeO}_2(\text{IRC})$ catalyst. The “S”, “O”, and “G” signals disappear when the spectrum is recorded at room temperature (Figure 4.c). The $4\%\text{Ag}/\text{CeO}_2(\text{WI})$ spectrum is composed of the three “C”, “O”, and “G” signals. However, the “O” signal with $g_{\perp} = 2.011$ is not well-resolved and disappears at room temperature (Figure 4.c). This indicates that the O_2^- is weakly adsorbed on the surface. The “G” signal is well resolved compared to the same signals recorded for the other catalysts. Indeed, it shows an axial symmetry characterized by $g_{\parallel} = 2.040$ and $g_{\perp} = 2.038$ with hyperfine coupling constants equal to $A_{\parallel} = 67$ G and $A_{\perp} = 24$ G. This signal is attributed to Ag^{2+} ions present in the solid.

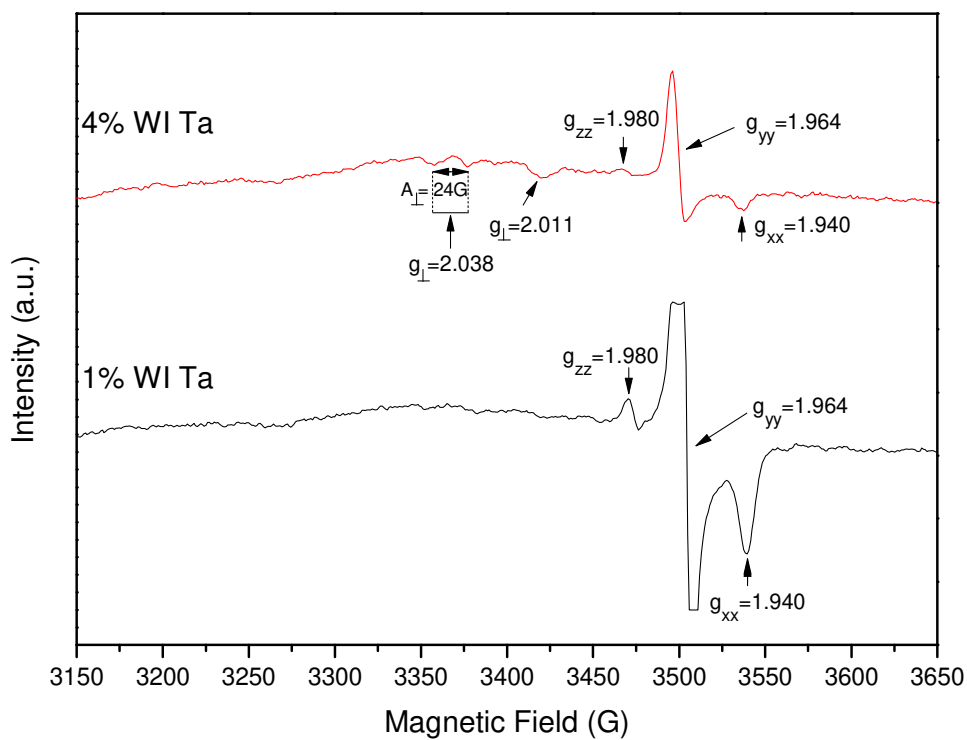
When the spectrum is recorded at room temperature, the “G” signal remains stable and its intensity decreases according to the Curie law. The higher resolution of “G” signal may be attributed to the lower amount of Ag^{2+} present in this sample. Indeed, lower interactions between paramagnetic Ag^{2+} species leads to more resolved signals. In fact, the reduction peak due to Ag^{2+} species (at 96°C) in TPR profile of 4%Ag/CeO₂(WI) is very small compared to the homologous ones in 4%Ag/CeO₂(IRC) and 4%Ag/CeO₂(DPU). The stability of the Ag^{2+} ions obtained for high silver content explains the enhanced performance in the catalytic oxidation of propylene [4] compared to the 1%Ag/CeO₂(WI) counterpart.



4.a



4.b



4.c

Figure 4: Electron paramagnetic resonance (EPR) spectra, recorded at ambient temperature, of x%Ag/CeO₂ catalysts (x = 1 or 4 wt%), a) (IRC), b) (DPU), and c) (WI).

4. Conclusion

Three different preparation methods are used to prepare catalysts Ag supported on CeO₂ (IRC, DPU, and WI, with 1 and 4 wt% Ag). The catalysts are evaluated in propylene total oxidation. The order of catalytic activity is: 4%Ag/CeO₂(IRC) > 4%Ag/CeO₂(WI) > 4%Ag/CeO₂(DPU) > 1%Ag/CeO₂(IRC) > 1%Ag/CeO₂(WI) > 1%Ag/CeO₂(DPU). TPR and EPR techniques allowed the identification of the type of silver species.

Presence of Ag²⁺ species is responsible for the improvement of the catalytic activity. Indeed, the absence of Ag²⁺ species in 1%Ag/CeO₂(DPU) may explain its lowest catalytic performance compared to all the other catalysts, for which Ag²⁺ species was detected by EPR. In addition, the low stability of Ag²⁺ species in 1%Ag/CeO₂(WI), as revealed by EPR, may be at the origin of its lower activity in propylene oxidation compared to 1%Ag/CeO₂(IRC). In fact, 1%Ag/CeO₂(IRC) showed catalytic performance closer to catalysts 4%Ag contents than to 1%Ag content. The existence and stability of Ag²⁺ species in 1%Ag/CeO₂(IRC) may explain this behavior.

All the 4%Ag contents samples show better activity towards propylene oxidation than their homologous 1%Ag, due to the presence of higher amount of Ag²⁺ (reduction peak at temperature lower than 100°C in TPR and Ag²⁺ signals in EPR), besides Ag⁺. Furthermore, EPR revealed the existence of Ag(0) on 4%Ag/CeO₂(IRC). The presence of the Ag²⁺, Ag⁺, and Ag⁰ species in the 4%Ag/CeO₂(IRC) catalyst allows an electronic interaction among three different redox couples: Ag²⁺/Ag⁺, Ag²⁺/Ag⁰, and Ag⁺/Ag⁰. The simultaneous presence of these redox couples may be the reason behind the superior catalytic activity of the 4%Ag/CeO₂(IRC) catalyst in the total oxidation of propylene compared to the catalysts comprising only the Ag²⁺/Ag⁺ redox couple. Finally, it is stated that Ag content and the preparation method are parameters influencing the catalyst performance in oxidation reactions by affecting the type and amount of silver species.

CRedit authorship contribution statement

S. Benaissa: Experiments, Investigation. **L. Cherif-Aouali:** Conceptualization, Investigation, Supervision, Funding acquisition. **S. Hany:** Experiments, Investigation, Contribution to the original draft. **M. Labaki:** Analysis, Editing. **S. Aouad:** Analysis, Editing. **R. Cousin:** Analysis, Editing. **S. Siffert:** Conceptualization, Investigation, Supervision, Funding acquisition. **A. Aboukaïs:** Writing original draft, Conceptualization, Investigation, Analysis, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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