

Effect of Ag, Cu, and Au Incorporation on the Diesel Soot Oxidation Behavior of SiO₂: Role of Metallic Ag

Grisel Corro · Umapada Pal · Edgar Ayala ·
Esmeralda Vidal · Emmanuel Guilleminot

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Abstract The catalytic behaviors of Ag, Cu, and Au loaded fumed SiO₂ have been investigated for diesel soot oxidation. The diesel soot generated by burning pure Mexican diesel in laboratory was oxidized under air flow in presence of catalyst inside a tubular quartz reactor in between 25 and 600 °C. UV–Vis optical spectroscopy was utilized to study the electronic states of Ag, Cu, and Au(M) in M/SiO₂ catalysts. The soot oxidation was seen to be strongly enhanced by the presence of metallic silver on 3 % Ag/SiO₂ surface, probably due to the formation of atomic oxygen species during the soot oxidation process. The catalyst is very stable due to the stability of Ag⁰ species on the catalyst surface and high thermal stability of SiO₂. Obtained results reveal that though the freshly prepared 3 % Cu/SiO₂ is active for soot oxidation, it gets deactivated at high temperatures in oxidizing conditions. On the other hand, 3 % Au/SiO₂ catalyst does not present activity for diesel soot oxidation in the conventional soot oxidation temperature range. The catalytic behaviors of the supported catalyst samples have been explained considering the electron donating ability of the metals to generate atomic oxygen species at their surface.

Keywords Diesel soot oxidation · Cu/SiO₂ · Ag/SiO₂ · Au/SiO₂ · Diesel emissions

G. Corro (✉) · E. Ayala · E. Vidal · E. Guilleminot
ICBUAP, Benemérita Universidad Autónoma de Puebla,
4 sur 104, 72000 Puebla, Mexico
e-mail: griselda.corro@correo.buap.mx

U. Pal
Instituto de Física, Benemérita Universidad Autónoma
de Puebla, Apdo. Postal J-48, 72570 Puebla, Mexico
e-mail: upal@sirio.ifuap.buap.mx

1 Introduction

Use of diesel-powered vehicles in the world has been increased considerably in recent years due to their lower fuel consumption and higher durability in comparison with gasoline-powered vehicles. Diesel engines are expected to play a positive role in the prevention of global warming through their higher fuel efficiency and lower CO₂ emissions than gasoline engines. However, there is a strong demand for the abatement of nitrogen oxides (NO_x) and particulate matter (PM; mainly soot) emerging from diesel engines which can give rise to environmental and health problems. The severity of new emission regulations requires solutions based on suitable after-treatment technologies, as well as technical improvements to the engines. The most effective and widely applied after-treatment technology for the control of particulate matter (PM) is based on diesel particulate filter (DPF) [1].

A catalyzed diesel particulate filter is regarded as the most promising solution to reduce PM emissions at lower exhaust temperatures (300–400 °C) [2]. However, large soot particles barely penetrate into the micropores or mesopores of the catalysts, and thus, catalytic soot oxidation is very slow due to the poor soot/catalyst contact [2]. To overcome this problem, a variety of catalysts and technologies based on different principles have been proposed.

The potentiality of silver deposited on Al₂O₃ for carbon particle oxidation in the presence of NO_x and oxygen has been demonstrated recently [3]. Aneggi et al. [4] have investigated the soot oxidation activity of Ag based catalysts deposited on Al₂O₃, CeO₂, and ZrO₂, demonstrating that the combustion of soot is promoted by Ag, especially in zero valent state, over the three supports. As the fumed SiO₂ presents a very high surface area (~550 m²/g), it can

increase the residence time and deposition rate of carbon particles over the catalyst surface, thereby increasing the probability of interaction between the carbon particles and the active sites of the catalyst, along with the active oxygen species produced on Ag surface. The above mentioned characteristics of silver and fumed SiO_2 lead us to investigate the behavior of Ag/ SiO_2 supported catalyst on the oxidation of diesel soot particles. As it has been demonstrated by several research groups [5, 6], the electron transfer from metal to O_2 is a key factor for the chemisorption of oxygen on a metal surface. The differences in the relative stabilities of different oxygen species on different metal surfaces are attributed to the differences in their electron donation abilities. In this study, we investigate the effect of the electron donating abilities of IB group metals like Cu, Ag, and Au, deposited over SiO_2 on the diesel soot oxidation process. UV–Vis absorption spectroscopy has been utilized to determine the oxidation state of the catalysts. While Ag-loaded fumed SiO_2 has been demonstrated as a stable, effective catalyst for diesel soot oxidation, Cu and Au loaded fumed SiO_2 have been found to be not active for this reaction. The catalytic behaviors of the supported catalysts have been correlated to the electronic state of the loaded metals.

2 Experimental

2.1 Preparation of the Catalysts

The catalysts were prepared by impregnation using an aqueous solution of 1 M silver nitrate (Aldrich 99.9 %) for the 3 % Ag/ SiO_2 , an aqueous solution of 1 M copper nitrate (Aldrich 99.9 %) for the 3 % Cu/ SiO_2 , and an aqueous solution of 0.1 M $\text{Na}(\text{AuCl}_4)$ (Aldrich 99.9 %) for the 3 % Au/ SiO_2 catalysts. After impregnation, the catalysts were dried at 50 °C overnight, and then dried in air for 6 h at 120 °C. The dried catalysts were reduced in pure hydrogen flow for 4 h at 500 °C. A reference SiO_2 support was prepared in the same way using only distilled water.

2.2 Characterization of the Catalysts

The elemental composition of the catalysts was determined through energy dispersive X-ray spectroscopy (EDS), utilizing a NORAN microanalysis system attached to a JEOL, JSM-6300 scanning electron microscope. Specific surface areas of the catalysts were determined from their N_2 physisorption isotherms at 77 K using BET analysis methods. The UV–Vis absorption spectra of the supported catalysts were obtained for the dry-pressed disk samples using a Varian Cary 500 UV–Vis spectrophotometer with DRA-CA-30I diffuse reflectance accessory using BaSO_4 as

standard reflectance sample. UV–Vis absorption spectroscopy is an easy, non-expensive technique which enabled us to determine the electronic state of metals like Ag, Cu, and Au in the supported catalysts before and after the soot oxidation reactions.

2.3 Soot Generation

Soot used in this study was generated by burning pure diesel fuel purchased from Mexican market in a glass vessel with an externally controlled air flow recirculation (Fig. 1). The exhaust gas of the vessel was directed to the powder catalyst sample (200 mg) placed inside a tubular quartz reactor (7 mm inner diameter) in a programmable furnace. The process was performed using an air feed volume flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$ consisting of 20 vol% of O_2 and 80 vol% of N_2 . The soot generated from the exhaust gas of the vessel, was accumulated for 1 h on the catalyst in the tubular reactor. In order to verify that combustion of the blends took place in lean conditions, oxygen feed volume flow in the vessel exhaust was monitored by gas chromatography. Oxygen flow remained higher than $10 \text{ cm}^3 \text{ min}^{-1}$ during the combustion process, indicating the presence of excess oxygen during diesel combustion process.

2.4 Temperature Programmed Soot Oxidation

After 1 h accumulation of diesel soot over the catalyst surface, air was purged for 15 min to perform soot oxidation. The air (20 vol% of O_2 and 80 vol% of N_2) feeding or flow rate was maintained at $100 \text{ cm}^3 \text{ min}^{-1}$. The mixture was heated in the 25–600 °C temperature range with $10 \text{ }^\circ\text{C min}^{-1}$ heating rate, and then cooled down to 25 °C.

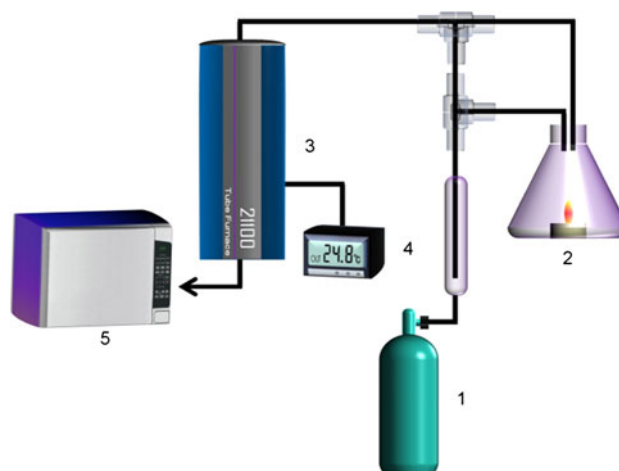


Fig. 1 Schematic diagram of the system used for monitoring the combustion process. 1 Air, 2 diesel burner, 3 reactor, 4 temperature controller, and 5 gas chromatograph

The process comprising soot accumulation on the catalyst at room temperature for 1 h, its subsequent oxidation at higher temperatures, and the cooling down process to 25 °C is called a cycle. After this first cycle, five similar cycles were performed over the same catalyst sample. CO₂ emissions from the reactor were analyzed by gas chromatography. The soot retained by the catalysts after 1 h of diesel combustion was about 8.45 mg (measured in a Shimadzu AX200 balance), attaining a soot/catalyst ratio of 0.042.

3 Results and Discussion

3.1 Catalyst Characterization

The catalyst characterization data are summarized in Table 1. It can be seen from the table that during the catalyst preparation, the high temperature H₂ reduction process in the presence of Cu, Ag or Au, resulted in a strong decrease in SiO₂ specific surface area. While during H₂ reduction of the catalysts, HNO₃ and HCl could be produced from the used metal precursors like AgNO₃, Cu(NO₃)₂ and Na(AuCl₄), which are strong enough acids to interact with SiO₂ particles causing a decrease of their specific surface area, possibility of formation metallic particles at the surface of silica at high temperature reduction might also be the cause for the reduction of specific surface area of the supported catalysts.

Figure 2 presents the UV–Vis absorption spectra for the 3 % Ag/SiO₂ catalyst before and after performing 6 soot oxidation cycles. It can be seen that: a broad signal spreading through 320 and 600 nm, which can be ascribed to the overlapping of Ag SPR signal (400–550 nm) with the σ – σ^* and n – σ^* transition signals of Ag_{*n*} clusters generally appear in the 330–360 and 440–540 nm spectral range, respectively [7, 8]. It can be seen that there are no differences between the absorption spectra of the sample before (Fig. 2a) and after diesel soot oxidation (Fig. 2b).

The result suggests that the electronic state of silver in 3 % Ag/SiO₂ remained the same even after six soot oxidation cycles.

Table 1 Catalysts characterization data

Catalyst	Metal content (wt%)	Specific surface area (m ² g ^{−1})	
		Fresh sample	After 6 oxidation cycles
SiO ₂	–	550	540
3 % Cu/SiO ₂	2.98	210	198
3 % Ag/SiO ₂	3.11	190	186
3 % Au/SiO ₂	3.05	195	190

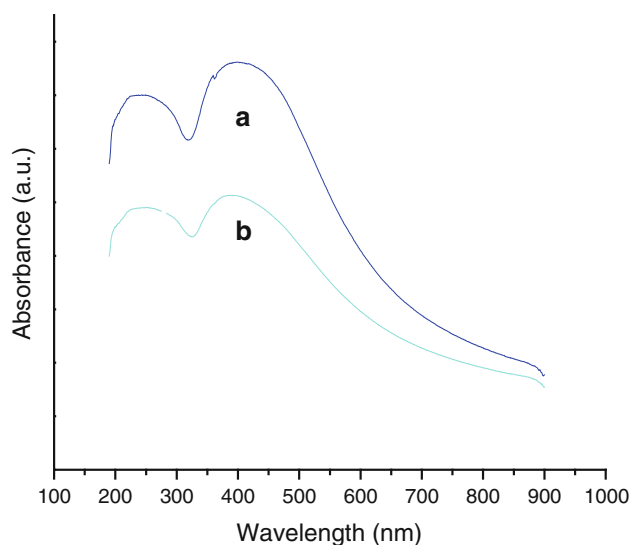


Fig. 2 UV–Vis absorption spectra of a fresh 3 % Ag/SiO₂, b 3 % Ag/SiO₂ after 6 oxidation cycles

In Fig. 3, the UV–Vis absorption spectra of the 3 % Cu/SiO₂ sample before and after its use in soot oxidation process (6 cycles) are presented. In the spectrum of the as prepared sample (curve a), the presence of a broad signal in the 220–360 nm spectral range (peaked at about 250 nm) can be assigned to the charge-transfer transition of the ligand O^{2−}, to isolated metal center Cu²⁺ and the d – d transition of CuO particles [9–11]. A broad signal spreading through 530 and 650 nm can be ascribed to the plasmonic absorption of metallic copper particles (peaked around 550 nm). In the spectrum b, it can be seen that this band disappeared almost completely after the diesel soot oxidation cycles. However, two new absorption bands at around 350 and 510 nm appeared. The band at around 350 nm corresponds to the transitions of Cu⁺ in Cu₂O, indicating the generation of

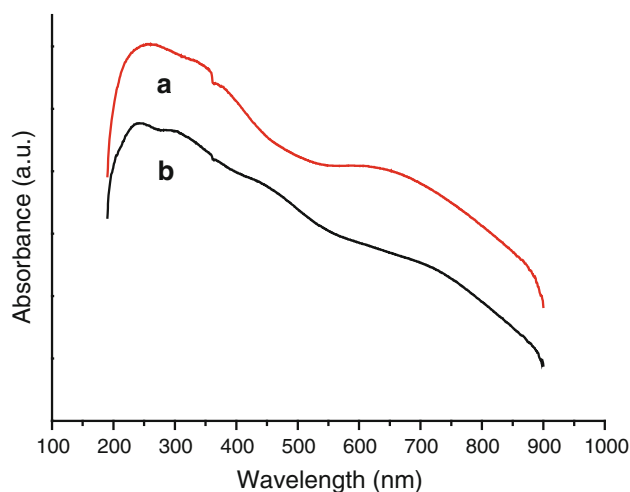


Fig. 3 UV–Vis absorption spectra of a fresh 3 % Cu/SiO₂, b 3 % Cu/SiO₂ after 6 oxidation cycles

Cu₂O layers on the particles surface [10]. The band around 510 nm can be assigned to the absorption of traces of metallic copper particles. These results suggest an oxidation of the Cu⁰ atoms present in the fresh sample to Cu⁺ during the diesel soot oxidation process.

The UV–Vis absorption spectra of the 3 % Au/SiO₂ catalyst before and after six diesel soot oxidation cycles (Fig. 4) revealed a broad signal spreading through 470 and 600 nm that can be ascribed to SPR absorption signal of metallic gold nanoparticles [12–14]. The spectrum showed that there are no appreciable differences between the absorption spectrum of the sample before and after the diesel oxidation cycles. The results suggest that the electronic states of gold in the fresh catalyst remained unaffected even after six soot oxidation cycles.

3.2 Soot Oxidation Over the Catalysts

In order to compare the effect of the catalysts on diesel soot oxidation, the oxidation cycle described in Sect. 2.4 was first performed over only quartz wool in the 25–800 °C temperature range. In the absence of an oxidation catalyst, very low amounts of CO₂ could be detected in between 25 and 600 °C. However, the CO₂ evolution curve as a function of temperature revealed a strong signal presenting a T_{max} at ~700 °C. The total area under the CO₂ evolution curve in between 25 and 800 °C determined over quartz wool is designated as [CO₂]_{qwool} and is taken as a measure of the total amount of carbon in the soot generated from the exhaust gas of the vessel. The catalytic efficiency of each catalyst is defined as:

$$\text{Catalyst efficiency} = \frac{[\text{CO}_2]_{\text{cat}}}{[\text{CO}_2]_{\text{qwool}}},$$

where [CO₂]_{cat} is the area under CO₂ curve (soot oxidation evolution in between 25 and 600 °C) measured over the catalyst, and [CO₂]_{qwool} is the area under CO₂ curve (soot oxidation evolution in between 25 and 800 °C) measured over quartz wool. The calculated catalytic efficiency values of the catalysts are reported in Table 2.

The results of soot oxidation experiments over SiO₂, shown in Fig. 5, revealed only a small signal at about 350 °C, and the intensity of the CO₂ evolution peak did not

Table 2 Efficiency values of the catalysts during the 1st, 2nd, and 6th oxidation cycles

Catalyst	Catalyst efficiency		
	1st	2nd	6th
SiO ₂	0.02	0.01	0.00
3 % Ag/SiO ₂	0.71	0.77	0.85
3 % Cu/SiO ₂	0.60	0.09	0.10
3 % Au/SiO ₂	0.01	0.00	0.00

vary appreciably from cycle to cycle. These results indicate that the SiO₂ is not active for oxidizing diesel soot.

Figure 6 shows the evolution of CO₂ as a function of the diesel soot oxidation temperature over 3 % Ag/SiO₂, for the 1st, 2nd and 6th soot oxidation cycles. As can be seen, the temperature of maximum soot oxidation (T_{max}) remained unaltered (~200 °C) during the six soot oxidation cycles. Moreover, the specific surface area of the catalyst remained unchanged even after six soot oxidation cycles (Table 1), and its catalytic efficiency does not vary much from cycle to cycle (Table 2). The results indicate that the catalyst is thermally stable under the used oxidation conditions.

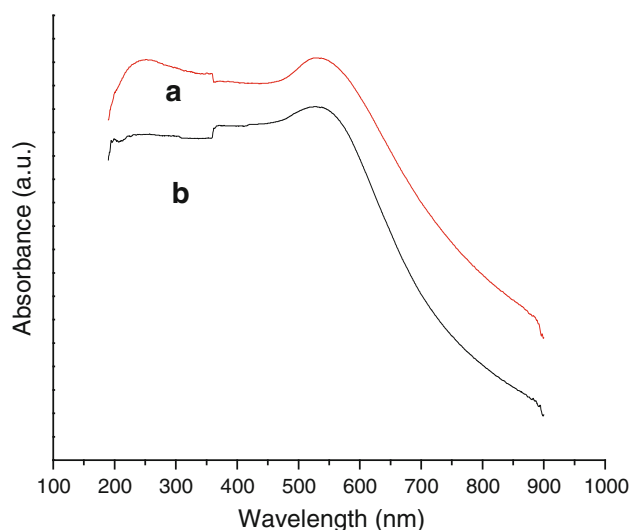


Fig. 4 UV–Vis absorption spectra of samples **a** Fresh 3 % Au/SiO₂, **b** 3 % Au/SiO₂ after 6 oxidation cycles

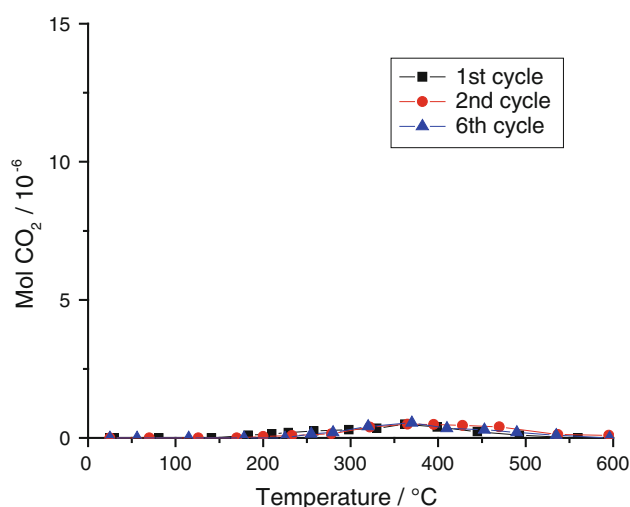


Fig. 5 Evolution of CO₂/g cat. as a function of soot oxidation temperature over SiO₂

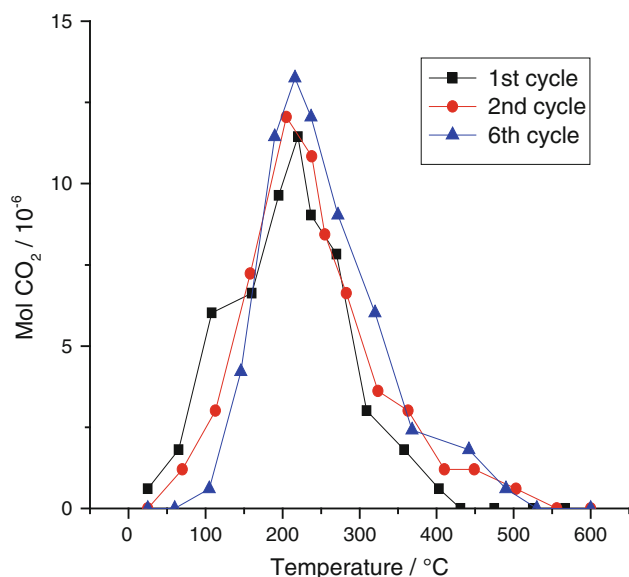


Fig. 6 Evolution of $\text{CO}_2/\text{g cat.}$ as a function of soot oxidation temperature, over 3 % Ag/SiO_2

Such characteristic of the oxidation cycles suggests that the structure of the catalyst remained unchanged during the diesel soot oxidation process. Therefore, the active silver present over the surface of the fresh catalyst remained in its reduced state during the soot oxidation cycles. This assumption is supported by the results obtained from the UV–Vis absorption spectra of the catalyst (Fig. 2) before and after 6 diesel soot oxidation cycles.

The evolution of CO_2 as a function of the diesel soot oxidation temperature over the 3 % Cu/SiO_2 catalyst is shown in Fig. 7. From the figure, we can see that for the first diesel soot oxidation cycle, CO_2 evolution curve revealed an intense signal at about 260 °C. However, this

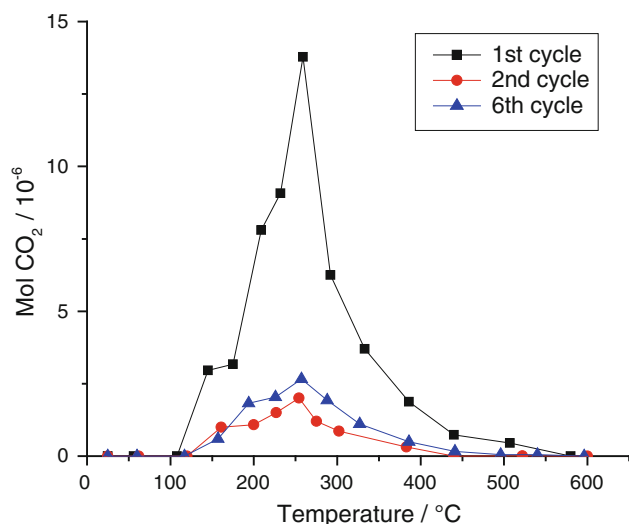


Fig. 7 Evolution of $\text{CO}_2/\text{g cat.}$ as a function of soot oxidation temperature, over 3 % Cu/SiO_2

signal disappeared almost completely during the subsequent reaction cycles.

These results and the catalytic efficiency values calculated for the three soot oxidation cycles over 3 % Cu/SiO_2 (Table 2) indicate that the catalyst was strongly deactivated during the first cycle of diesel soot oxidation. The result can be explained assuming that the high temperature and excess oxygen present during the process might have generated a change in the electronic states of copper sites on the catalyst, converting them as non-active sites for diesel soot oxidation.

This assumption is supported by the results obtained from the UV–Vis absorption spectra of the catalyst before and after the reaction cycles (Fig. 3). Absorption spectrum of the catalyst before soot oxidation reaction revealed the presence of Cu^0 , which can generate the superoxide O_2^- ions, the highly active species well known for improving the oxidation of diesel soot [3, 4]. The absorption spectrum of the catalyst after six reaction cycles shows a drastic reduction of the signal in between 530 and 650 nm, corresponding to the Cu^0 plasmon adsorption, and the appearance of the signals at 350–510 nm, ascribed to Cu_2O . As is well known, Cu_2O is not active for the activation of oxygen adsorption [15]. It is interesting to note that in the spectrum b of Fig. 3, there appeared a band around 510 nm, which can be assigned to the absorption of traces of metallic copper particles. Appearance of 510 nm band in the sample indicates that despite being in strong oxidation conditions during the six soot oxidation cycles, copper can exist in metallic (particulate) form. These metallic particles may be active for soot oxidation, and might be responsible for the residual activity of the catalyst during 2nd–6th reaction cycles as appeared in Fig. 7. This assumption is supported by the constant values of T_{max} observed for the six soot oxidation cycles.

The effect of temperature on diesel soot oxidation over 3 % Au/SiO_2 catalyst revealed that for the first soot oxidation cycles, CO_2 evolution is low (a very low signal at about 300 °C in the CO_2 evolution curve, results not presented). These results and the catalytic efficiency values calculated for the three soot oxidation curves over the catalyst (Table 2) indicate that the catalyst is rather inactive for diesel soot oxidation. It must be noted that the UV–Vis spectra of the catalyst (Fig. 4) before and after diesel soot oxidation cycles were almost unchanged in characteristics, revealing that the gold remained in its zero valent state even after 6 soot oxidation cycles.

The results obtained from the present investigation demonstrate that 3 % Ag/SiO_2 is a very potent soot oxidation catalyst. It is, in fact, well known that metallic silver is an oxidation catalyst that can form several suboxide species (oxygen ad-molecule, superoxide ion, subsurface oxygen, oxygen adatoms, and oxidic oxygen adatoms) in

oxidation atmosphere. Gaseous oxygen might be adsorbed on the surface of metallic Ag particles to form atomic oxygen species, which are the first active oxygen species for soot oxidation, although there remains the possibility forming other oxygen species. The electron transfer from the metal to O₂ is the principal factor for the chemisorption of oxygen on metal surfaces, and this electron transfer depends on the ionization energy of the metal. As the first ionization energy values for Cu and Ag are 7.72 and 7.57 eV, respectively [16], the electron donating ability of these metals to adsorbed oxygen (forming atomic oxygen species) should be similar: therefore, we can expect similar catalytic activities of Cu and Ag for soot oxidation. However, our results showed that while the 3 % Ag/SiO₂ catalyst presents a strong activity for soot oxidation during six consecutive reaction cycles, the 3 % Cu/SiO₂ catalyst gets deactivated during the first soot oxidation cycle, probably due to the formation of Cu₂O species at the high oxidation temperature (600 °C). Indeed, the standard enthalpy change of formation of CuO₂ is larger (−168.6 kJ/mol) compared with that of Ag₂O (−31.05 kJ/mol).

4 Conclusions

The results obtained in this investigation indicate that 3 % Ag/SiO₂ is a highly potent supported catalyst for diesel soot oxidation at low temperatures (150–300 °C). The catalyst is highly stable at the conventional diesel soot oxidation temperature range (25–600 °C) during multiple consecutive reaction cycles. The metallic silver in the catalyst acts as active species during the soot oxidation reaction, promoting the formation of atomic oxygen at catalyst surface, the key factor in the diesel soot oxidation process. Presence of the atomic oxygen species improves the contact, and increases the probability of electronic interaction between the catalyst surface and the solid diesel soot particles. On the other hand, though the presence of

Cu⁰ species in 3 % Cu/SiO₂ catalyst can promote the production of adsorbed atomic oxygen species, formation of Cu₂O at high reaction temperature leads to a strong deactivation of the catalyst for soot oxidation. Finally, due to very high ionization energy of gold, it cannot generate of the adsorbed atomic oxygen species at its surface due to the difficulty in transferring electrons from Au⁰ to O₂, and hence, the 3 % Au/SiO₂ remains inactive in the conventional temperature range of diesel soot oxidation.

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