

Low Cost Cu/ZnO as Low Temperature (150 °C) Catalyst for Diesel Particulate Matter Oxidation

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Abstract The catalytic behavior of hydrogen-reduced copper loaded ZnO, SiO₂, and TiO₂ has been investigated for diesel particulate matter (PM) oxidation. 5 %Cu/ZnO showed a strong diesel PM oxidation activity at 150 °C. XPS spectroscopy was utilized to study the electronic states of Cu in Cu/ZnO catalyst. Presence of Cu¹⁺ ions at the surface of the catalyst even after its use in PM oxidation cycles was assigned responsible for its high catalytic performance. The high stability of Cu¹⁺ is explained on basis of the isoelectronic interactions of Cu¹⁺ (3d¹⁰) with Zn²⁺ (3d¹⁰) at the Cu₂O–ZnO interface. Cu/SiO₂ and Cu/TiO₂ were not active for this reaction probably due to the absence of Cu¹⁺ which could not be stabilized by Ti⁴⁺ or Si⁴⁺. Results indicate that 5 %Cu/ZnO catalyst can be utilized for the abatement of diesel engine emissions even from the starting point of cold engines.

Keywords Diesel particulate matter oxidation · Cold diesel engine emissions · Cu/ZnO oxidation catalysts

1 Introduction

Particulate matter (PM) emitted from diesel engines has caused acute human health and environmental problems [1]. A wall flow filter is normally employed to trap the However,

to keep the back pressure of the engine low, the filter needs frequent regeneration by burning the trapped PM at high temperatures, which often damage the filter. A self-regenerable PM filter is thus needed to reduce the emissions. A key challenge of this technology is to develop a catalyst that can accelerate the PM oxidation at low temperature as much as possible [2]. During the last few years, several catalytic systems have been investigated for this purpose, and the diesel PM oxidation temperature could be reduced to 200–400 °C [3] using these new catalysts. However, as far as our knowledge goes, PM oxidation at temperatures lower than 200 °C has not been achieved.

Most of the oxidation catalysts available in market are based on noble metals (Pt, Pd, and Rh), which are highly expensive. Therefore, in the present work, we have utilized hydrogen reduced Cu/ZnO, Cu/TiO₂, and Cu/SiO₂ composites as catalysts for diesel PM oxidation, exploiting the interactions of transient and non-transient active copper species generated during its processing steps. The structural and electronic properties of the catalysts were studied utilizing X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (Cu2p3/2, CuL3MM) techniques. The catalytic behavior of the catalysts in diesel PM oxidation performed between 25 and 600 °C was correlated with their physicochemical properties, considering the contributions of active and non-active species like Cu⁰, Cu¹⁺, and Cu²⁺ present on their surface.

2 Materials and Methods

2.1 Catalysts Preparation

ZnO, TiO₂, and SiO₂ supplied by Merck (99.99 %) were used as support materials for the preparation of the Cu

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catalysts. The catalysts were prepared by impregnation using an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ to incorporate a nominal 5 %Cu in them. After drying, the catalysts were reduced in pure hydrogen flow for 4 h at 450 °C. Catalysts reduction was performed, in order to study the evolution of Cu^0 , Cu^{1+} , and Cu^{2+} species on the catalyst surface and their contribution on the diesel PM oxidation. Metallic unsupported copper particles (Baker, 99.9 %, 0.59–1.00 mm) and CuO (Baker, 99.9 %, 0.59–1.00 mm) were also used as reference catalysts.

2.2 Catalysts Characterization

Adsorption measurements were performed using a Quantachrome Nova-1000 sorptometer. Specific surface areas were measured by N_2 physisorption at 77 K using BET analysis methods.

XPS were recorded on the freshly prepared hydrogen reduced 5 %Cu/ZnO catalyst, after its sixth PM oxidation cycles, using an Escalab 200R electron spectrometer equipped with a hemispherical analyzer, operating in a constant pass energy mode. Monochromatic $\text{MgK}\alpha$ emission ($h\nu = 1253.6$ eV) from the X-ray tube operated at 10 mA and 12 kV was utilized for recording XPS spectra of the samples.

2.3 Generation of PM

The particulate matter used in this study was generated by burning Mexican diesel in a glass vessel, under controlled air flow as described in our previous work [4]. The emission from the exhaust of the vessel was directed to the catalyst sample (200 mg) placed inside a tubular quartz reactor (inner diameter 10 mm) in a programmable furnace. The process was performed using an air feed volume flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$. The particulate matter generated from the exhaust gas of the vessel, was accumulated for 1 h on the catalyst.

2.4 PM Oxidation

After 1 h accumulation of diesel PM over the catalyst surface, air was purged for 15 min to perform PM oxidation. The air (20 vol% of O_2 and 80 vol% of N_2) feeding or flow rate was $100 \text{ cm}^3 \text{ min}^{-1}$. 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. The process comprising PM accumulation on the catalyst at room temperature for 1 h, its subsequent oxidation at increasing temperature 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. CO_2 emissions from the reactor were analyzed by gas chromatography.

3 Results and Discussion

3.1 Characterization of the Catalysts

The catalyst characterization data are summarized in Table 1. As can be seen, all the samples did not change significantly after using them in PM oxidation.

3.2 Characterization of Catalysts by XPS and Auger Spectroscopy

The binding energies of the Cu $2p_{3/2}$ core-level emissions from Cu^{1+} and Cu^0 are essentially the same, appearing at about 1.4 eV below that of Cu^{2+} ions, thus, the identification of both reduced copper species (Cu^{1+} and/or Cu^0) in solid catalysts is very difficult by considering XPS data alone [5]. To identify these two copper species in our catalysts, we monitored their L_3VV X-ray induced Auger emissions (AES). For this purpose, the modified Auger parameter (α_A) was defined as:

$$\alpha_A = h\nu + \left(\text{BE Cu}2p_{3/2} - \text{BE Cu}_{\text{L}3\text{MM}} \right)$$

where $h\nu$ is the energy of the incident photon (1253.6 eV) and the expression in parenthesis represents the difference between the binding energy of the Cu $2p_{3/2}$ photoelectron ($\text{BE Cu } 2p_{3/2}$) and the binding energy of the L_3VV Auger emission ($\text{BE Cu}_{\text{L}3\text{MM}}$). The α_A is an empirical measure with a unique value for each Cu species (Cu^{1+} , Cu^{2+} , and Cu^0) and can be used as a fingerprint for characterizing such species. The values of α_A and the binding energies of Cu $2p_{3/2}$ levels of the fresh reduced catalyst, and after its use in the sixth oxidation cycle of PM oxidation are compiled in Table 2.

The hydrogen reduced 5 % Cu/ZnO catalyst, before using it in PM oxidation, shows a binding energy (BE) of the $\text{Cu}2p_{3/2}$ emission of 932.7 eV (Fig. 1). This BE value and the absence of satellite line somewhere around 941 eV preclude the presence of Cu^{2+} ions. In other words, copper species must be either as Cu^0 and/or Cu^{1+} . The L_3VV Auger spectrum of the sample suggests that both Cu^0 and/or Cu^{1+} are present; although the metallic phase is dominant. On the other hand, the catalyst, after six PM oxidation cycles, displays the BE of the $\text{Cu}2p_{3/2}$ level at 934.1 eV

Table 1 Catalyst characterization data

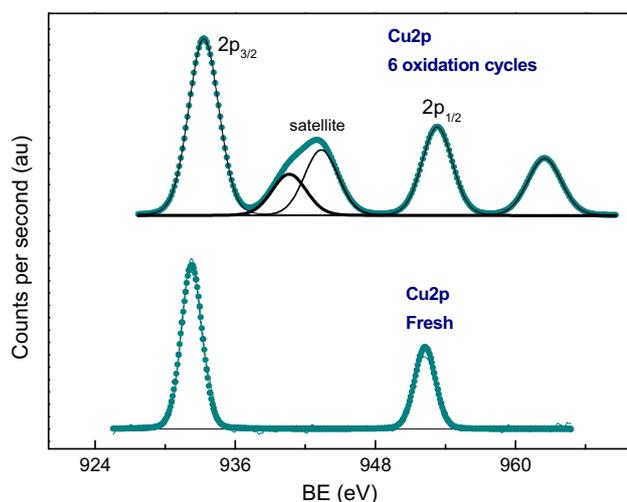
Catalyst	Specific surface area ($\text{m}^2 \text{ g}^{-1}$)	
	Fresh sample	After six oxidation cycles
5 % Cu/ZnO	3.31	3.25
5 % Cu/ TiO_2	15.26	13.55
5 % Cu/ SiO_2	80.55	75.89

Table 2 Binding energies (eV), Auger parameter (α_A) at the surface of the catalysts

Catalyst	Cu2p _{3/2}	α_A (eV)
5 % Cu/ZnO fresh	932.7	1849.2
		1851.0
5 % Cu/ZnO after six cycles	934.1	1849.1
		1851.1
5 % Cu/TiO ₂ fresh	932.6	1851.0
5 % Cu/TiO ₂ after six cycles	934.2	1851.3
5 % Cu/SiO ₂ fresh	932.7	1851.0
5 % Cu/SiO ₂ after six cycles	934.2	1851.2

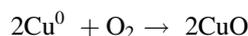
together with the intense satellite line. Both facts indicate that copper remains essentially as CuO. This assignment is confirmed by the α_A at 1851.1 eV with a minor contribution at 1849.1 eV, indicating that the major CuO species coexists with a minor proportion of Cu¹⁺.

In Table 2, it can be also observed the values of α_A and the binding energies of Cu 2p_{3/2} levels of the fresh reduced 5 %Cu/SiO₂ and 5 %Cu/TiO₂ catalysts, and after their use in the sixth oxidation cycle of PM oxidation. Fresh 5 %Cu/SiO₂ and 5 %Cu/TiO₂, showed BE of the Cu2p_{3/2} emission of 932.7 and 932.6 eV respectively, suggesting that copper species are either Cu⁰ and/or Cu¹⁺. However, the α_A calculated for both samples correspond to Cu⁰ with no Cu¹⁺ contribution. Both catalysts, after six PM oxidation cycles, display the BE of the Cu2p_{3/2} level at 934.2 eV indicating that copper remained as CuO. This fact is confirmed by the α_A at 1851.2 eV of 5 % Cu/SiO₂ and 1851.3 of 5 % Cu/TiO₂ indicating the presence of only CuO species, with any proportion of Cu¹⁺.

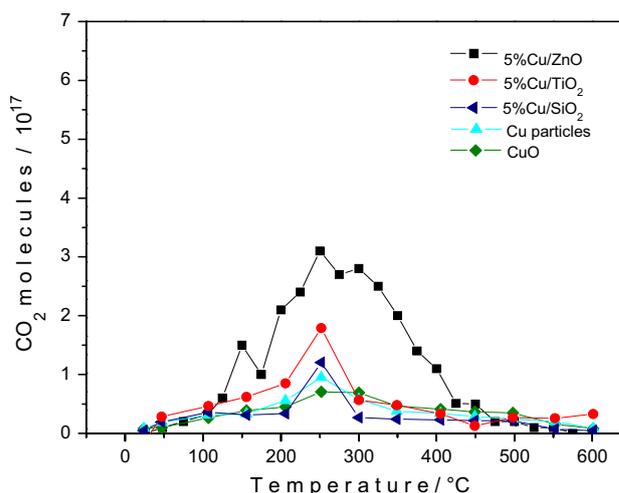
**Fig. 1** Cu2p_{3/2} core level XPS spectrum of 5 % Cu/ZnO

3.3 PM Oxidation over the Catalysts

The evolution of CO₂ as a function of PM oxidation temperature during the first reaction cycle over (1) metallic unsupported copper particles, (2) commercial CuO, (3) 5 % Cu/ZnO, (4) 5 %/TiO₂, and (5) 5 % Cu/SiO₂ is shown in Fig. 2. Figure 3 shows the evolution of CO₂ as a function of PM oxidation temperature during the sixth reaction cycle over the same catalysts. In Fig. 2 it can be seen that over fresh metallic unsupported copper particles, there is a strong CO₂ signal at about 250 °C, which disappeared almost completely during the oxidation cycles, indicating a complete deactivation of the catalyst, as shown in Fig. 3. The effect is expected as the electronic state of metallic copper changes at high temperature under excess oxygen flow utilized for PM oxidation, converting most of the active metallic catalytic sites to non-active sites for diesel PM oxidation according to the reaction:



This assumption is confirmed by the evolutions of CO₂ as a function of the PM oxidation temperature during the first and sixth cycles over CuO presented in Figs. 2 and 3, which show a very low CO₂ signal evolution for this catalyst. The high activity presented by metallic unsupported copper particles, for the first PM oxidation cycle can be associated to the presence of Cu⁰ which might have promoted the formation of superoxide ions (O₂⁻) resulting in an enhancement of the PM oxidation rate, in a similar way to that proposed to explain the high PM oxidation activity of Ag⁰ in Ag/SiO₂ [4]. Figure 2 shows the temperature evolution of CO₂ during the first PM oxidation over 5 %Cu/ZnO. It can be seen a broad signal spreading through 200–550 °C which can be assigned to the

**Fig. 2** Evolution of CO₂ molecules as a function of PM oxidation temperature over the catalysts during the first cycle

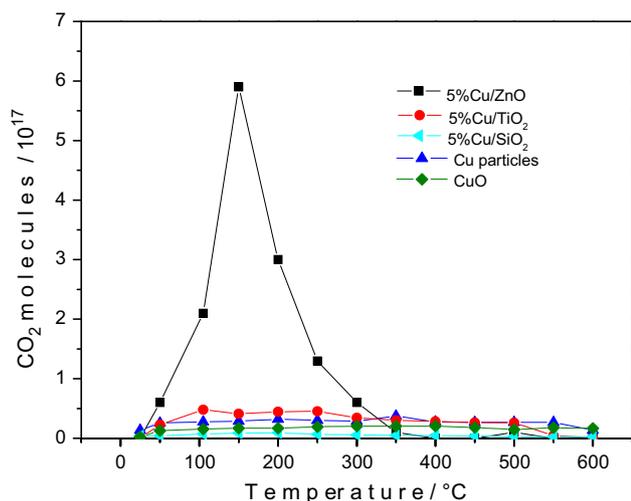


Fig. 3 Evolution of CO₂ molecules as a function of PM oxidation temperature over the catalysts during the sixth cycle

overlapping of two signals: a signal at about 250 °C arising from the PM oxidation over metallic copper, (as was demonstrated for the PM oxidation over metallic unsupported copper particles), and another signal at about 300 °C associated to the PM oxidation over other catalytic sites created probably during the catalyst reduction.

It is interesting to note a small signal which appeared at about 150 °C. This signal was not detected during PM oxidation over the other copper catalysts (metallic unsupported copper particles and CuO). Now, the catalyst composition determined by the core level XPS spectra, and the values of the Auger parameter α_A revealed the presence of Cu⁰, Cu²⁺, and Cu¹⁺ species in the hydrogen reduced 5 % Cu/ZnO catalyst before its use in PM oxidation process, however, the observed CO₂ evolution signal at about 150 °C cannot be associated to the PM oxidation over Cu⁰ sites, as they present oxidation activities at higher temperatures (250 °C). This signal can neither be associated to the PM oxidation over Cu²⁺ species, since CuO is inactive for the reaction. We assign CO₂ evolution signal detected at 150 °C to the PM oxidation over Cu¹⁺ ions present in the hydrogen reduced composite catalyst. As has been demonstrated earlier, the freshly prepared hydrogen reduced 5 %Cu/ZnO sample contains Cu¹⁺ ions, revealing Auger parameter α_A of 1849.2 eV corresponding to Cu₂O.

It is worth noting that the PM used in this study contains both the insoluble (carbon) and soluble organic fraction SOF components. We associate the CO₂ evolution peak detected at 150 °C to the catalytic oxidation of both the SOF and insoluble carbonous components over the composite catalyst through Cu¹⁺ active species. In fact there appeared no other peak of CO₂ evolution by extending the PM oxidation temperature up to 800 °C (results not shown) while using our composite catalyst. We believe that the

oxidation of the insoluble carbon of PM in close contact with Cu¹⁺ ions is promoted by the exothermic heat of SOF catalytic oxidation at the surface of the catalyst particles.

In Fig. 3, it can be observed that the intensity of the CO₂ evolution signal attributed to PM oxidation over Cu¹⁺ increased strongly, suggesting an increase of Cu¹⁺ concentration at the catalyst surface. An enhanced oxidation of SOF at the Cu¹⁺ sites of the catalyst along with the promoting effect of the exothermic heat of SOF oxidation might be the reasons for the higher CO₂ evolution signals observed in the sixth oxidation cycle.

The CO₂ evolution signals detected at about 250 °C for the first cycle (due to particulate matter oxidation on Cu⁰) decrease gradually from cycle to cycle due to the oxidation of metallic copper at the surface of the catalyst. Cu⁰ species present in the catalyst get oxidized to Cu¹⁺ during the oxidation cycles following the reaction:



Following this equation, the concentration of Cu¹⁺ species over the catalyst surface increases in expense of Cu⁰ on repeating the oxidation cycles, increasing CO₂ evolution at 150 °C, and suppressing the signal at 250 °C. The conclusion is supported by the Auger parameter reported in Table 2, which shows for the 5 % Cu/ZnO catalyst after six PM oxidation cycles, a dominant L₃VV contribution, whose Auger parameter fits the expected value for Cu₂O (1849.1 eV). The high stability of Cu¹⁺ ions in the severe oxidation conditions of PM oxidation cycles can be understood considering the isoelectronic interactions between Cu¹⁺ (3d¹⁰) with Zn²⁺ (3d¹⁰) at the Cu₂O–ZnO interface as has been explained by Herman et al. [6].

On the other hand, the catalyst, after six PM oxidation cycles, displays the BE of the Cu2p_{3/2} level at 934.1 eV together with the intense satellite line. Both facts indicate that copper remains essentially as CuO. This assignment is confirmed by the L₃VV contribution, whose Auger parameter fits the value for CuO (1851.1 eV) with a minor contribution at 1849.1 eV, indicating that the major CuO species coexists with a minor proportion of Cu¹⁺.

Now, in Fig. 2, it can be seen that both 5 %Cu/TiO₂ and 5 %Cu/SiO₂ showed a signal at about 250 °C arising from the PM oxidation over metallic copper, as was demonstrated for the PM oxidation over metallic unsupported copper particles. This signal disappeared almost completely during the oxidation cycles indicating a complete deactivation of the catalysts as shown in Fig. 3, probably due to the complete oxidation of Cu⁰ to Cu²⁺. It is worth noting that no signal at around 150 °C was detected during the PM oxidation cycles probably due to the absence of Cu¹⁺ which could not be stabilized during the oxidation cycles by isoelectronic interactions with Ti⁴⁺ or Si⁴⁺. This

suggestion is supported by the values of α_A and of the binding energies of Cu $2p_{3/2}$ levels of the 5 % Cu/TiO₂ and 5 % Cu/SiO₂, catalysts presented in Table 2. Fresh 5 % Cu/SiO₂ and 5 % Cu/TiO₂, showed BE of the Cu $2p_{3/2}$ emission of 932.7 and 932.6 eV respectively, suggesting that copper species are either Cu⁰ and/or Cu¹⁺. However, the α_A of both samples corresponds to Cu⁰ (1851.0 eV) with no Cu¹⁺ contribution. Both catalysts, after six PM oxidation cycles, display the BE of the Cu $2p_{3/2}$ level at 934.2 eV indicating that copper remained as CuO. This fact is confirmed by the α_A at 1851.2 eV of 5 % Cu/SiO₂ and 1851.3 of 5 % Cu/TiO₂ indicating the presence of only CuO species, which are inactive for the diesel PM oxidation.

4 Conclusions

A low cost, high performance catalyst for diesel PM oxidation could be synthesized by hydrogen reduction of Cu loaded ZnO powders. Using the catalyst, the oxidation temperature of diesel PM in air could be lowered to 150 °C. The catalyst can be used for the abatement of

diesel engine emissions even from the starting moment of a cold engine.

The results obtained from diesel PM oxidation activity and electronic state analysis of incorporated copper in the composite catalyst suggest that Cu⁰ and the Cu¹⁺ sites at the catalyst surface act as active species for PM oxidation due to their favorable electronic configuration.

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References

1. Knauer M, Schuster ME, Su D, Schlögl R (2009) *J Phys Chem A* 113:13871–13879
2. Bueno-Lopez A (2014) *Appl Catal B* 146:1–9
3. Doggali F, Grasset F, Cador O, Rayalu S, Teraoka Y (2014) *J Environ Chem Eng* 2:340–343
4. Corro G, Pal U, Ayala E, Vidal E, Guilleminot E (2013) *Top Catal* 56:467–472
5. Martin L, Martinez H, Poinot D, Pequenard B, Le Cras F (2013) *J Phys Chem* 117:4421–4430
6. Herman RG, Klier K, Simmons GW, Finn BP, Bulko JB (1979) *J Catal* 56:407–429