ZIRCONIA-SUPPORTED COPPER AND KNO_3 CATALYSTS FOR DIESEL SOOT COMBUSTION. DEACTIVATION BY HYDROTREATMENT AND SO_2

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Abstract

In this study, the sulfur tolerance and hydrothermal stability of Cu-KNO_3/ZrO_2 catalysts in catalytic diesel soot oxidation were investigated. Supported alkaline nitrate catalysts have shown excellent activity for soot oxidation in the presence of O_2 or NO/O_2. High-temperature water vapor treatments do not affect the catalytic activity, suggesting a good hydrothermal stability of the catalysts. Treatments performed at high SO_2 concentration lead to a partial deactivation of the catalysts for the combustion reaction in the presence of O_2. The presence of copper improves the sulfur tolerance of the KNO_3/ZrO_2 catalyst for the combustion of soot in the presence of NOx. NO/O_2 present in the feed flow of the reactor can regenerate *in situ* nitrate anions that provide the redox cycles required for the reaction.

Keywords: Diesel soot, combustion, hydrothermal stability, SO_2.

1. INTRODUCTION

The emissions of diesel engines contain pollutants such as liquids (unburned diesel fuel and lubricating oils), gases (NOx, SOx, residual hydrocarbons, low volatile organic compounds, and semivolatile organic compounds) and solids (as well as soot particles). Given that these emissions are harmful to both human health and the environment, the US and European standards require the reduction of all three phases of diesel emissions.

A diesel particulate filter (DPF), which is a cordierite structure where soot is trapped while the gaseous components pass unrestricted, may be used to remove the solid fraction. A DPF may contain an oxidation catalyst to assist in the combustion of trapped soot.

Suitable formulations to be used as catalysts have been widely studied in the last decade [1-13]. One line of study involves the use of catalysts of alkaline metal nitrates supported on oxides. The soot combustion with potassium nitrate supported on zirconia occurs in a low temperature range (250–410ºC) [14-15]. Then, it is interesting to investigate the behavior of these catalysts in the presence of deactivating substances such as water vapor or sulfur compounds.

Water vapor, present in the gas flow, can produce the loss of the active species by "washing" or dissolution, especially if the high temperatures at which the exhaust pipe operates are considered.

Sulfur present in emissions as SO_2 may poison the active sites. As required by the current standards, diesel fuel should have a low sulfur content, for instance, 15 ppm of sulfur in the United States specifications and 10 ppm of sulfur in the European Union specifications [16]. With these concentrations in the fuel, the concentration of SO_2 in the emissions is expected to be 1–3 ppm. There are few reports in the literature tending to show the deactivation or stability of diesel soot oxidation catalysts [17-22]. The deactivation phenomenon depends on the concentration of SO_2, temperature and the presence of other reactants in the poison mixture.

In this paper we study the activity, hydrothermal stability and resistance to sulfur poisoning of copper and potassium nitrate catalysts supported on zirconia used in the catalytic combustion reaction of diesel soot.

2. EXPERIMENTAL

2.1. Catalyst preparation

The hydrated zirconium oxide ($ZrO_2.nH_2O$) was obtained by hydrolysis of zirconium oxychloride, $ZrOCl_2.6H_2O$ (Fluka). The necessary amount of ammonium hydroxide (Tetrahedron, 28%) was added to the zirconium oxychloride to reach a pH = 10. The product obtained by hydrolysis was filtered and washed until it was free from chloride ions, as determined by the silver nitrate test. The hydrous zirconium ($ZrO_2.nH_2O$) thus obtained was dried at 80ºC for 24 h.

Catalysts were prepared by the impregnation of hydrous zirconium with an aqueous solution of $Cu(NO_3)_2$ and/or KNO_3, using the necessary amount of solution to fill the pore volume of the support. The precursors were dried at 80ºC for 24 h.

Catalysts were prepared with 10% potassium nitrate and 5% copper nitrate, and the concentrations are expressed as grams of nitrate ion or grams of copper in 100 grams of catalyst.

2.2. Poisoning with SO_2

Catalysts were poisoned *ex situ* with sulfur dioxide (SO_2) using an electrically heated fixed bed reactor. The feed mixture was obtained from two individually controlled feed lines: SO_2/N_2 and N_2 to close the balance. The SO_2 concentration used was 1000 ppm (Q total=30 ml/min). In the poisoning experiments, the loaded mass was 100 mg and treatments were carried out at 600ºC for 2 h. In order to name SO_2-treated catalysts, the letter "S" is used between parentheses in the nomenclature, for example KNO_3/ZrO_2(S).

2.3. Deactivation by hydrotreatments

Hydrotreatments were carried out on samples of fresh catalyst loaded in a quartz reactor fed with an inert (He) gaseous current (Q_{Total}= 30 ml/min) saturated with water vapor (10% vol.) at 600ºC for 5 h. In order to name hydrotreated catalysts, the letter "h" is used between parentheses in the nomenclature, for example KNO_3/ZrO_2(h).

2.4 Characterization

Crystalline phases within the catalysts were identified by powder X-ray diffraction (XRD) analysis using a Rigaku D-Max III diffractometer equipped with Ni-filtered Cu Kα radiation (λ = 1.5378 Å).

The presence of nitrate, nitrite, sulfate and sulfite anions in the catalysts was studied by means of FTIR spectroscopy using Bruker equipment.

2.5 Catalytic tests

2.5.1 Measurements of catalytic activity with an air mixture in a thermogravimetric reactor

The activity of fresh, hydrotreated and SO_2-treated catalysts was measured with a thermogravimetric technique. The soot combustion in the presence of air was made in a thermogravimetric reactor using a thermobalance (TGA-50 Shimadzu) with a heating rate of 10^{o}C/min and an air/He feed (60 cm^3 min^{-1}). The mixture composition was: 8% O_2 and helium for balance. In order to carry out activity experiments, the soot and the catalyst, in a 1/10 ratio, were milled before introduction into the reactor. The soot mass loss and the temperature were recorded as a function of time. The derivative curve (DTG) was obtained from the mass loss information as a function of time. Tmax is the temperature value that corresponds to the maximum combustion rate.

2.5.2. Measurements of catalytic activity with NO/O_2/He mixture

Catalytic tests were performed in a temperature programmed oxidation (TPO) apparatus, a quartz microreactor on-line with a reaction gas analyzer. The fixed bed microreactor was constructed in quartz (id = 0.8 cm) and heated electrically. The reaction mixture was obtained from three individually controlled feed lines: NO/He, O_2/He, and He to close the balance. To study the soot combustion reaction the reactor was fed with the following mixture: 1500 ppm of NO and 8% of O_2 (Q total = 50 ml/min). The microreactor was loaded with 30 mg of catalyst and 3 mg of soot (Printex–U) and the combustion was carried out in the range 200–600^{o}C with a heating rate of 2°C/min. Before the reaction, the soot was mixed with the catalyst-with a spatula (loose contact). The reaction products were monitored with a gas chromatograph, Shimadzu model GC-8A, provided with a TCD detector. The sampling was carried out approximately every 8 min. The separation of products was performed with a concentric column CTR I (Alltech). This system permitted the identification and quantification of the O_2, $N_{2,}$ $CO_{2,}$ and CO peaks. The concentration of CO_2 and CO was determined from the area of the CO_2 and CO peaks obtained by chromatographic analysis.

3. RESULTS

3.1. Characterization of fresh catalysts

The crystalline structure of the catalysts was determined by powder X-ray diffraction. The XRD patterns are shown in Figure 1. The pattern of the KNO_3/ZrO_2 catalyst showed a mixture of monoclinic (2 theta = 28.2º, 31.5º, 34.5º) and tetragonal phases (2 theta = 30.5°; 35.2°; 50.7°; 60.3°; 63.2°). Cu/ZrO_2 and Cu-KNO_3/ZrO_2 catalysts presented only the tetragonal phase of zirconia.

The crystalline phase of the copper oxide (2 theta = 38.5°; 35.3°; 48.6°; 61.4°; 67.9°) was only observed in the Cu-KNO_3/ZrO_2 catalyst. Probably in the Cu/ZrO_2 catalyst the crystals are small and cannot be observed by this technique.

Figure 1: X-ray diffraction patterns. (a) ZrO_2; **(b)** KNO_3/ZrO_2; **(c)** Cu/ZrO_2; **(d)** KNO_3-Cu/ZrO_2

The lines associated with the presence of crystalline KNO_3 (2 theta = 25.06; 31.1; 27.86; 36.05) were not clearly evident on the XRD patterns of the catalysts KNO_3/ZrO_2 or Cu-KNO_3/ZrO_2. No lines associated with the presence of K_2O (2 theta = 28.87; 31.13; 31.70, 36.7) were observed.

Spectroscopic techniques were used to corroborate the presence of nitrate species in the catalysts. The FTIR technique was used for qualitative purposes and energy absorption in the UV-Vis spectrum, for quantitative purposes.

Figure 2 shows the FTIR spectra of KNO_3/ZrO_2 and Cu-KNO_3/ZrO_2 fresh catalysts. Both spectra present antisymmetric N-O stretching bands typical of free nitrate ions (1385 cm^{-1}) [23]. These results suggest that part of the impregnated potassium nitrate remains in the catalyst as nitrate ion.

Figure 2: FTIR spectra of fresh catalysts: a) KNO_3/ZrO_2; b) Cu/ZrO_2; c) Cu-KNO_3/ZrO_2.

Table 1: Potassium and nitrate ion content in the catalysts

Catalyst	Nominal content		Experimental	
	% K	% NO_3^-	% K	% NO_3^-
KNO_3/ZrO_2	8.5	13.6	7.2	8
KNO_3-Cu/ZrO_2	8.5	13.6	9.1	12.7

In both catalysts, the potassium content is slightly different from the theoretical value. Nitrate ion content is lower than the nominal content in the KNO_3/ZrO_2 catalyst and similar to the nominal content in the Cu-KNO_3/ZrO_2 catalyst. These results indicate that part of the supported salt remains in the catalyst, and part of the salt is decomposed during calcinations, generating potassium oxide species (K_2O). The presence of copper generates stability of nitrate species and this result is in agreement with that obtained by FTIR spectra which shows that the band at 1385 cm^{-1} is more intense in the Cu-KNO_3/ZrO_2 catalyst than in the KNO_3/ZrO_2 catalyst.

3.2. Activity of catalysts

3.2.1. Results of the activity of fresh, poisoned and hydrotreated catalysts obtained in the thermogravimetric reactor

Figure 3 shows the curves of diesel soot combustion with fresh catalysts and the curve obtained in the absence of catalyst. This figure especially shows the derivatives of the TGA curve as a function of temperature. Table 2 lists the maximum combustion rate temperature (Tmax) and includes the Tmax obtained with the SO_2-treated and hydrotreated catalysts.

Figure 3: Curves of diesel soot combustion in fresh catalysts a) KNO_3/ZrO_2; b) Cu/ZrO_2; c) Cu-KNO_3/ZrO_2 y soot.

Table 2: Catalyst activity in the thermogravimetric reactor

Catalyst	Tmax (°C) Fresh	Tmax (°C) SO_2-treated	Tmax (°C) Hydrotreated
Diesel soot (Printex-U)	610	-	-
KNO_3/ZrO_2	400	517	389
Cu/ZrO_2	460	510	495
KNO_3-Cu/ZrO_2	380	493	390

The combustion of diesel soot in the absence of catalyst occurs at high temperature (Tmax = 610 °C). In the presence of the fresh catalysts, this temperature decreases substantially. The catalysts that are more active are those that contain potassium nitrate. As reported previously, nitrate ions participate in the combustion of diesel soot with a nitrate-nitrite redox cycle [11-13].

$$2\ NO_3^- + C \rightarrow CO_2 + 2\ NO_2^- \qquad \text{(eq. 1)}$$

$$2\ NO_2^- + O_2 \rightarrow 2\ NO_3^- \qquad \text{(eq. 2)}$$

While the Cu/ZrO_2 catalyst exhibits poor activity, the addition of oxidic phases of copper to the KNO_3/ZrO_2 catalyst generates a promoter effect of activity. The most active catalyst is Cu-KNO_3/ZrO_2. This catalyst is the one with a higher content of potassium nitrate.

The high-temperature steam treatment results in a loss of activity in the catalyst Cu/ZrO_2. On the other hand, the catalysts that contain potassium nitrate, KNO_3/ZrO_2(h) or Cu-KNO_3/ZrO_2 (h), show good activity. This activity was attributed to the stability of the nitrate species, which remain in the hydrotreated catalysts. FTIR spectra of Cu-KNO_3/ZrO_2(h) and KNO_3/ZrO_2(h) catalysts (Figure 4) showed the presence of bands associated with nitrate species.

Figure 4: FTIR spectra of hydrotreated catalysts: a) KNO_3/ZrO_2 (h); b) Cu/ZrO_2 (h); c) Cu-KNO_3/ZrO_2 (h).

Table 3 lists the Tmax obtained in the combustion reactions of diesel soot in the presence of fresh and SO_2 *ex situ* treated catalysts. Pretreatments of catalysts with SO_2 were performed using severe conditions: high concentrations of SO_2 (1000 ppm) and high temperature (600°C). This temperature is higher than that found in the exhaust pipe (150–450ºC) and the activity results, obtained with SO_2-treated catalysts, show evidence of deactivation. KNO_3/ZrO_2 and Cu-KNO_3/ZrO_2 catalysts exhibit a significant activity decrease after poisoning. The KNO_3/ZrO_2 catalyst is the most affected, its Tmax increasing up to 517°C. The Cu/ZrO_2 catalyst does not show an important deactivation and consequently it can be stated that the SO_2 treatment causes an activity loss that could be related to the disappearance of nitrate catalytic sites. The FTIR spectra of KNO_3/ZrO_2(S) and Cu/ZrO_2(S) catalysts (Figure 5) do not show bands associated with nitrate species.

Figure 5: FTIR Spectra of SO_2-treated catalysts: a) KNO_3/ZrO_2 (S); b) Cu/ZrO_2 (S); c) Cu-KNO_3/ZrO_2(S).

On the other hand, the FTIR spectrum of the Cu-KNO_3/ZrO_2(S) catalyst shows a weak band at 1385 cm^{-1} that is associated with NO_3^- ions. In addition, the spectra of poisoned catalysts show an intense band in the zone of 1114 cm^{-1} that can be attributed to the antisymmetric stretching of the S-O bond of sulfate ions. Potassium might have affinity with SO_2 and potassium nitrate could react with SO_2 to form potassium sulfate, K_2SO_4 (eq.3).

$$2\ KNO_3 + SO_2(g) \leftrightarrow K_2SO_4 + 2\ NO_2(g) \qquad \Delta\ G°(600°C)=-170{,}980\ kJ \ \text{(eq. 3)}$$

Potassium oxide species (K_2O) can react with the SO_2 to form potassium sulfite, K_2SO_3 (eq.4).

$K_2O + SO_2(g) \leftrightarrow K_2SO_3$ Δ G°(600°C)=-318,643 kJ (eq. 4)

However, the FTIR bands associated with the presence of sulfite ions (1220 and 980 cm^{-1}) are not observed in the spectra.

3.2.2. Results of the activity of fresh and SO_2-treated catalysts obtained in a fixed bed reactor fed with NO/O_2

Table 3 lists the Tmax obtained during soot combustion in a flow reactor using a feed mixture that contained 8% O_2 in the presence of NO (1500 ppm) using fresh and sulfur-treated catalysts.

Table 3: Tmax obtained using fresh and poisoned catalysts in the presence of NO.

Catalyst	Tmax (ºC) Fresh catalyst	Tmax (ºC) Poisoned catalyst
Diesel soot	590	-
KNO_3/ZrO_2	390	495
Cu/ZrO_2	410	455
KNO_3-Cu/ZrO_2	395	430

Fresh catalysts show excellent activity and the soot oxidation temperature decreases more than 200ºC compared with the combustion without catalyst. It can be noticed that $KNO_3/ZrO_2(S)$ catalysts show lower activity than the fresh one. The maximum combustion rate for the treated catalyst occurs approximately at 100^{o}C above the temperature of the fresh catalyst. The SO_2 treatment affects the activity of the catalysts that contain copper, $Cu/ZrO_2(s)$ and Cu-$KNO_3/ZrO_2(s)$ to a lesser degree and have activity in the temperature range of the exhaust pipe (temperatures lower than 450ºC). The presence of copper improves the sulfur tolerance of the KNO_3/ZrO_2 catalyst in the presence of NOx.

NO/O_2 present in the feed flow of the reactor can regenerate, *in situ*, nitrate anions for example, from K_2O or copper species. Ciambelli et al. [24] have noted that soot oxidation activity of a V/Cu/C/Ti-containing catalyst decreases with the sulfur pretreatment, but this decrease is minor when NO is added to the gas phase.

4. CONCLUSIONS

Zirconia- supported alkaline nitrate catalysts have shown excellent activity for soot oxidation in the presence of O_2 or NO/O_2.

FTIR spectra of KNO_3/ZrO_2 and Cu-KNO_3/ZrO_2 fresh catalysts present energy absorption bands associated with the presence of free nitrate ions and these ions participate in the combustion of diesel soot with a nitrate-nitrite redox cycle.

High-temperature water vapor treatments do not affect the catalytic activity. Hydrotreated catalysts that contain potassium nitrate show good activity and their FTIR spectra showed the presence of bands associated with nitrate species.

KNO_3/ZrO_2 and Cu-KNO_3/ZrO_2 catalysts exhibit a significant activity decrease after SO_2 poisoning in the presence of O_2 and the activity loss can be related to the disappearance of nitrate catalytic sites.

NO/O_2 present in the feed flow of the reactor can regenerate *in situ* nitrate anions that provide the redox cycles required for the reaction.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

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CAPTIONS

Figure 1: X-ray diffraction patterns. (a) ZrO_2; **(b)** KNO_3/ZrO_2; **(c)** Cu/ZrO_2; **(d)** KNO_3-Cu/ZrO_2.

Figure 2: FTIR spectra of fresh catalysts: a) KNO_3/ZrO_2; b) Cu/ZrO_2; c) Cu-KNO_3/ZrO_2.

Figure 3: Curves of diesel soot combustion in fresh catalysts a) KNO_3/ZrO_2; b) Cu/ZrO_2; c) Cu-KNO_3/ZrO_2 y soot.

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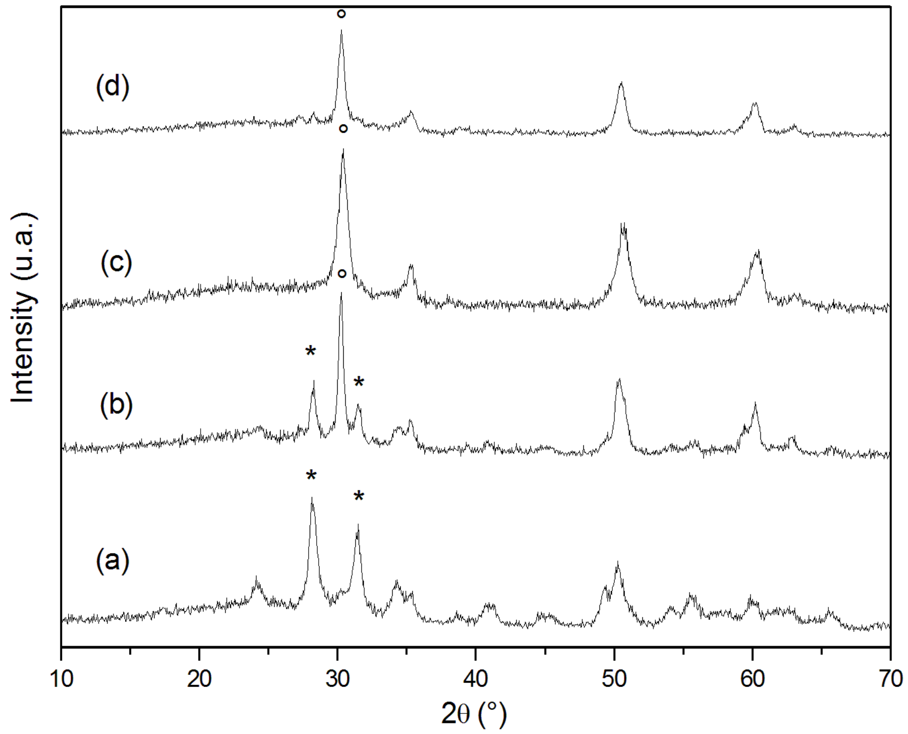
FIGURES



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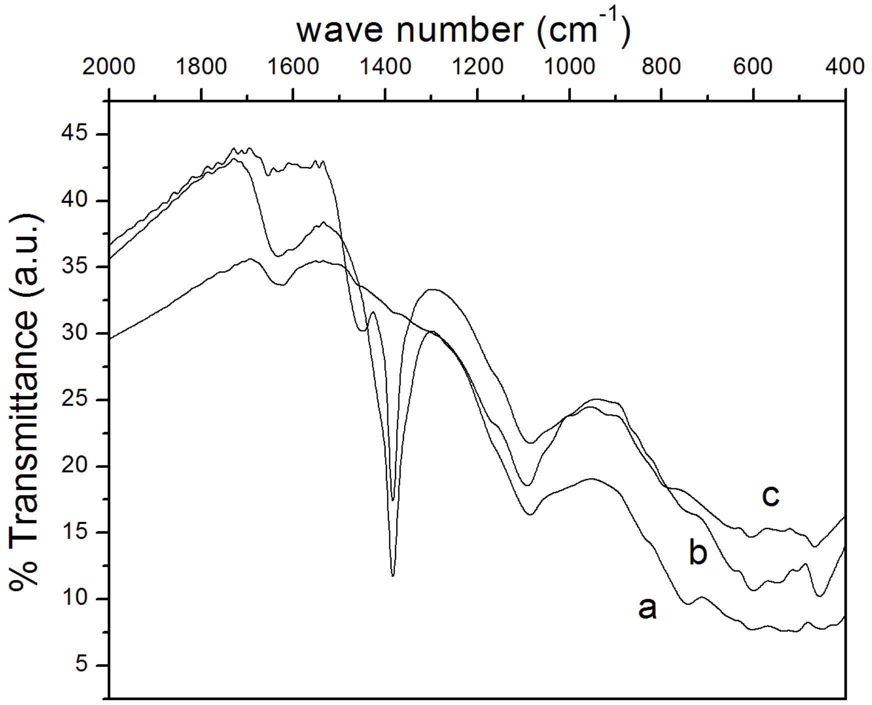
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Figure 2

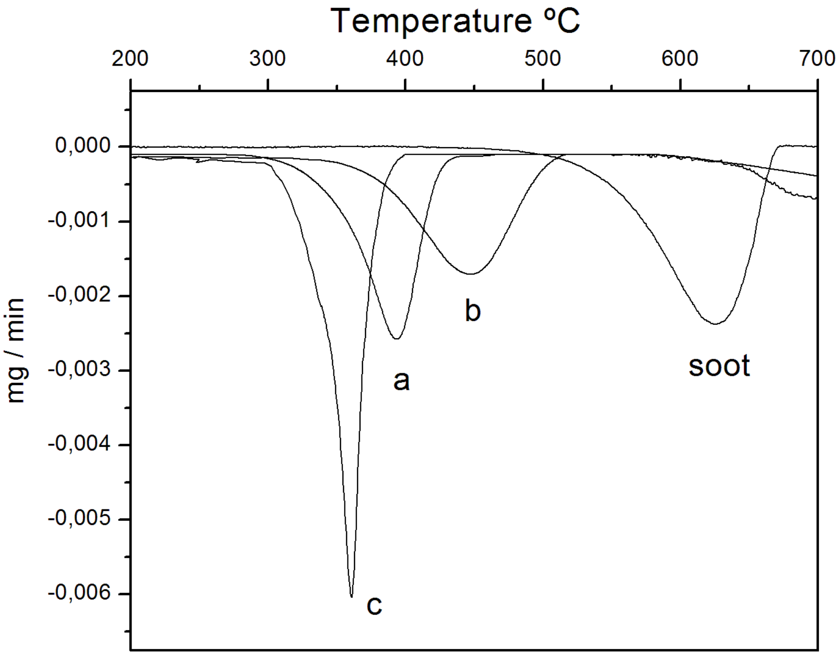

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Figure 3

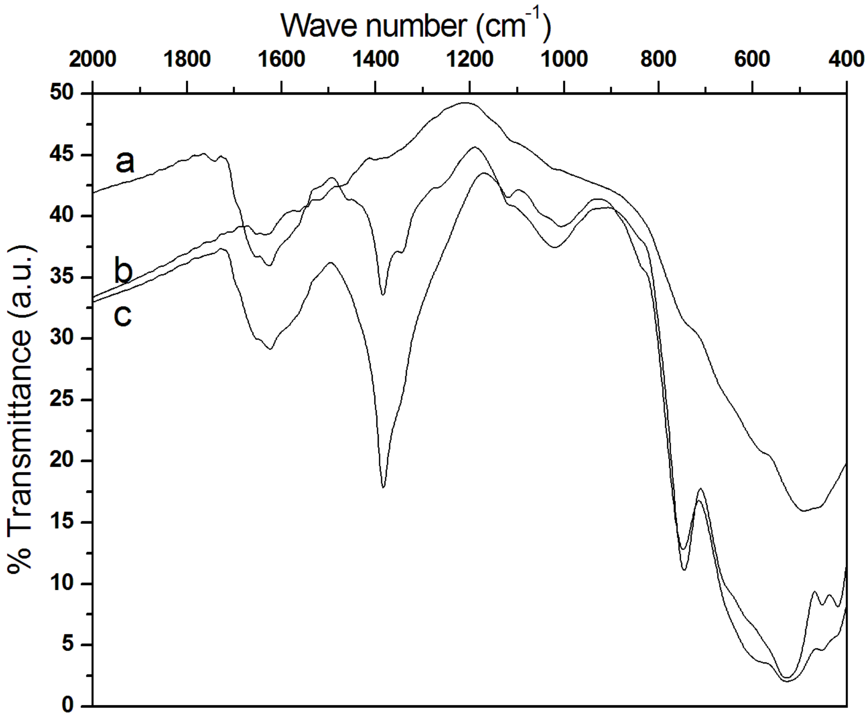
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Figure 4

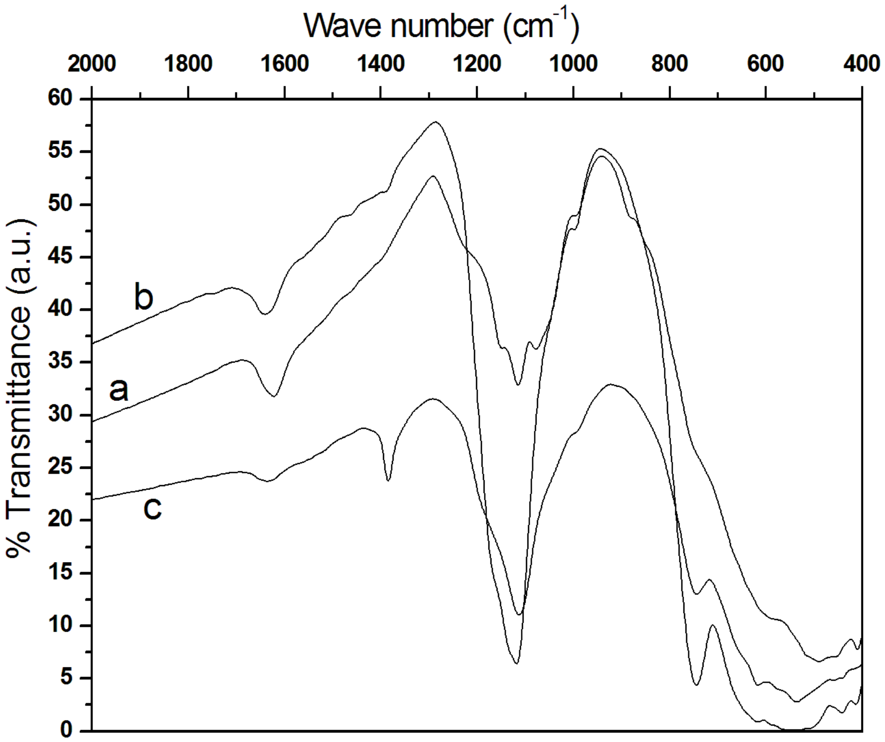
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Figure 5