

# Preparation and Characterization of Copper and/or Cerium Catalysts Supported on Alumina or Ceria

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## Abstract

Catalysts combined from (Al, Ce, and Cu) were prepared by impregnating copper, cerium nitrates, or both of them onto alumina in order to decrease the diesel soot by complete oxidation. The specific surface area of these catalysts changes by about 8% between the calcination temperature of 300°C and 500°C. However, it greatly decreases beyond 500°C. It has been noted that, when impregnating copper and cerium on alumina, copper has a higher effect upon the specific area compared to cerium's effect, and that the nitrates' decomposition on alumina takes place in temperature ranging between 200°C and 400°C. It has been also noted that, when reducing these catalysts at different temperatures with an atmosphere of hydrogen, the more the percentage of copper is higher in the catalysts, the more easily the copper oxide reduces. The use of CeO<sub>2</sub> as a support, decreases the reduction temperature of copper oxide Cu<sup>+2</sup> compared to Al<sub>2</sub>O<sub>3</sub>. However, copper is modified with cerium CuCe/Al<sub>2</sub>O<sub>3</sub> the CeO<sub>2-x</sub> has no effect on the reduction temperature of Cu<sup>+2</sup>.

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**Keywords:** CuO; CeO<sub>2</sub>; Al<sub>2</sub>O<sub>3</sub>; Sol-gel method; impregnation; specific area; Thermogravimetry;

## 1. Introduction

The vast development of industry and the increasing demands for human needs lead unintentionally to the increase of environmental pollution. For such reasons the concerned authorities have begun issuing strict laws which enforce industries to reduce the prevalent pollution which is the result of their factories or the engines which they manufacture. The European Union strict laws, for example, enforced automobile industry to reduce the amounts of prevalent soot pollutants emitted from the road vehicles. Therefore since 1993 petrol cars use in their exhaust effective catalysts which decrease the rate of pollution caused by these engines. The catalysis system has now extended to diesel vehicles. Hence the purpose of this study is to prepare and characterize catalysts formed from CuO, CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

The oxides of transition metals combined with other oxides such as that of zinc, chrome, thorium and cerium have been extensively studied [1-3], and the catalytic properties of these catalysts are the result of active centres surrounded by an electronic hole, the ability of the hydroxyl roots to move on the surface of the catalyst and finally the catalyst capacity to store hydrogen or oxygen in its structure. These properties are the outcome of the nature of the support and the conditions in which the catalysts are handled and activated. Cerium oxide has been

widely used as a support [4-5] because it has two oxidation numbers: Ce<sup>+3</sup> and Ce<sup>+4</sup>, which enable it to form non-stoichiometric oxides CeO<sub>2-x</sub> [6-9].

The lack of oxygen in this type of oxides leads to the formation of electronic holes which makes these oxides semi-conductors. But in fact these holes are capable of easily receiving or giving oxygen, and play a role as a regulator of existing oxygen in the catalysts used in petrol exhaust cars [10-12].

It has been revealed that the presence of cerium delays the glassing process of active phase in catalysts and improves the stabilities of aluminum oxide  $\gamma$  at high temperatures [13-14]. Aluminum oxide is also used as a support in various catalysts especially when its specific area is high [15-17].

## 2. Experimental Work

### 2.1. Catalysts preparation :

Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) and cerium oxide (CeO<sub>2</sub>) were prepared in order to use them as supports.

#### 2.1.1. Preparation of Al<sub>2</sub>O<sub>3</sub> :

Al<sub>2</sub>O<sub>3</sub> has been prepared by (Sol-gel methods) which can be carried out as follows:

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1.  $\text{Al}(\text{O}-\text{C}_4\text{H}_9)_3$  was dissolved in butanol-2 as solvent by the ratio three volumes from butanol-2 to one volume from  $\text{Al}(\text{O}-\text{C}_4\text{H}_9)_3$ . We shake it well at the temperature of  $80^\circ\text{C}$  till complete dissolution at about 15 minutes.
2. A double amount of butane-diol 1-3 was added to the two previous mixtures at the temperature  $60^\circ\text{C}$  and shake it. Then we obtain a white complex.
3. A distilled water was added to the previous complex at 10 volume of water to 1 from  $\text{Al}(\text{O}-\text{C}_4\text{H}_9)_3$  at the temperature of  $60^\circ\text{C}$  and shake it at about 30 minutes, until a precipitate aluminum hydroxide is formed.
4. The precipitate was cooled and evaporated under lightened pressure, then a wet white powder of hydroxide  $\text{Al}(\text{OH})_3$  was gotten. then the powder was dried in a furnace at a temperature of  $100^\circ\text{C}$  for 24 hours air atmosphere.
5. The powder was calcinated at the temperature of  $500^\circ\text{C}$  with a current of air or oxygen for six hours, then aluminum oxide was obtained with specific surface area (BET) of about  $420 \text{ m}^2/\text{g.cata}$ .

### 2.1.2. Preparation of Support $\text{CeO}_2$ :

1. 65 g of Cerium nitrates  $\text{Ce}(\text{NO}_3)_3$  was dissolved in 1 L of distilled water to obtain a solution of 0.2 mol/L. The dissolution was added to 1L of ammoniac 10%, then there will be a light yellow precipitate of cerium hydroxide  $\text{Ce}(\text{OH})_3$  which can be separated by filtering. This will produce a brownish powder.
2. The powder was put into a drying furnace at the temperature of  $100^\circ\text{C}$  for 24 hours under air atmosphere.
3. The powder was calcinated at  $500^\circ\text{C}$  with a current of air for 6 hours.

### 2.1.3. Preparation of Catalysts:

At first two catalysts were prepared with certain atomic percentages.

1.  $\text{Ce}/\text{Al} = 0.1$ ,  $\text{Cu}/\text{Al} = 0.1$ ; it is identified as  $1\text{Cu}1\text{Ce}10\text{Al}$ .
2.  $\text{Ce}/\text{Al} = 0.1$ ,  $\text{Cu}/\text{Al} = 0.5$ ; it is identified as  $5\text{Cu}1\text{Ce}10\text{Al}$ . And in order to examine the interaction between these three metals, we prepared two catalysts composed of two metals (Cu, Al) with different atomic percentages.
3.  $\text{Cu}/\text{Al} = 0.1$ ; it is identified as  $1\text{Cu}10\text{Al}$ .
4.  $\text{Cu}/\text{Al} = 0.5$ ; it is identified as  $5\text{Cu}10\text{Al}$ . Two catalysts composed of two metals were also prepared, the first was (Ce, Al) and the other was (Cu, Ce).
5.  $\text{Ce}/\text{Al} = 0.1$ ; it is identified as  $1\text{Ce}10\text{Al}$
6.  $\text{Cu}/\text{Ce} = 1$ ; it is identified as  $1\text{Cu}1\text{Ce}$

Three oxides formed from (Ce, Cu, Al) have been prepared by impregnating cerium and copper nitrates simultaneously on aluminium oxide ( $\text{Al}_2\text{O}_3$ ), which has been prepared by getting a gel substance.

#### The methods for preparing these catalysts:

1. Cerium nitrates and copper nitrates were dissolved in as little distilled water as possible (concentration about 1 mol/L) by the following ratios:  $\text{Cu}/\text{Al} = 0.1$  and  $\text{Ce}/\text{Al} = 0.1$  and once more  $\text{Cu}/\text{Al} = 0.5$  and  $\text{Ce}/\text{Al} = 0.1$ .
2. An amount of the dissolution was added whose volume is little bigger than that of the pores of aluminium oxide (the volume of the pores of aluminium oxides is 2.3

ml/g) and (the volume of the pores of cerium oxides is 0.4 ml/g).

3. The mixture was evaporated in a sand-bath at about  $100^\circ\text{C}$  until we get a saturated dissolution.
4. The remnants of nitrates were added to the saturated dissolution while shaking at various goes in order to get a paste.
5. The paste was dried in a furnace at  $100^\circ\text{C}$  for 24 hours under air atmosphere. It was in the same way that we were impregnated copper nitrates into  $\text{Al}_2\text{O}_3$  with the ratio of  $\text{Cu}/\text{Al}$  was 0.1 and once more 0.5.

It was the same way of preparing  $1\text{Cu}1\text{Ce}$ , but the support was changed to  $\text{CeO}_2$ . The catalysts were calcinated at various temperatures:  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $700^\circ\text{C}$  and then at  $800^\circ\text{C}$  to examine the influence of different calcinations temperature on the specific surface area.

### 2.2. Studying the loss of mass at various temperatures (Thermogravimetry):

This study has been conducted via an apparatus with a very sensitive balance of microgram brand (SARTORIUS4433MP8). This balance has two dishes, we place in one a small quartz carpula containing 40 to 50 mg of the samples. In the other dish we place an empty quartz carpula that equilibrate the weight electronically with the other dish by a computer. This group can be heated at a temperature from  $20^\circ\text{C}$  to  $800^\circ\text{C}$  under a current of various gases. The changes of the mass can be followed via a computer.

### 2.3. Specific area calculation:

In an attempt to calculate the specific area we used the method (BRAUNAUER, EMMET, TELLER) BET, which depends on the calculation of the amount of physically adsorbed nitrogen on the catalyst's surface at the liquid temperature of nitrogen -  $196^\circ\text{C}$ . This study has been conducted via an apparatus (QAEANTASORB).

## 3. Results and Discussion

### 3.1. Specific Area

The results in Table 1 include the values of the specific areas of different catalysts calcinated at various temperatures. We note from this table that the specific area is changed slightly between  $300^\circ\text{C}$  and  $500^\circ\text{C}$ . This can be accounted by the happening of a better crystallization process between these temperatures. But after temperature  $500^\circ\text{C}$  the catalyst begins to frit. This will be accompanied by a stark decrease of specific area. But as for the catalysts  $1\text{Cu}1\text{Ce}$ , we note that the specific area continually decreases with the rise of calcination temperature until it reaches the value  $9 \text{ m}^2/\text{g.cata}$  at temperature  $800^\circ\text{C}$ . This value agrees with the value of the specific area of copper oxide  $\text{CuO}$  obtained when we measured it on its own.

Table(1) The changes of the specific area B.E.T with different calcination temperature degrees from 300°C to 800°C.

Calcination temperature	5Cu1Ce10Al	1Cu1Ce10Al	5Cu10Al	1Cu10Al	1Ce10Al	1Cu1Ce
300 °C	155	248	128	296	346	110
400 °C	160	242	136	261	316	95
500 °C	158	232	136	261	316	72
600 °C	128	201	137	237	262	57
700 °C	-	168	-	217	-	28
800 °C	53	96	56	98	185	9

If we compare the catalysts 5Cu10Al with 1Cu10Al, we note that the increase of the percentage of copper leads to a great decrease of specific area, and the presence of cerium in these catalysts reduces the percentage of diminution of the specific area, as we have seen for the two catalysts 5Cu1Ce10Al and 1Cu1Ce10Al. We also note that copper has a great effect on specific area in comparison with cerium 1Cu10Al and 1Ce10Al.

### 3.2. Studying of Thermogravimetry:

#### 3.2.1. Oxide State:

The catalysts have been studied via the loss of mass apparatus with the following conditions:

The temperature used was between the room temperature degree and 800°C. The increase of the temperature was programmed at a speed of 1°C/min from the room temperature up to 800°C under a current of air whose rapidity was 4L/h. Figure 1 reveals the percentage of the loss of mass with temperature for the sake of catalysts (1Cu1Ce10Al, 5Cu1Ce10Al). Figure 2 shows the percentage of the loss of mass with temperature degree for the sake of catalysts (5Cu10Al, 1Cu10Al). A comparative look at these curves in the figures below indicates that we can divide them into three regions:

#### First region:

It is from normal temperature to temperature 180°C. It represents the release of physically adsorbed water, and the water of crystallization from the catalyst's surface. The percentage of loss of mass will range from 11 to 17%.

#### Second region:

It is from temperature 180°C to 400°C. It represents the decomposition of nitrates. as follows:



#### Third region:

It is from 400°C to 800°C. It almost represents the stage of stability of the mass. The theoretical loss of mass when the nitrates are decomposed can be calculated in terms of the final mixture form ( $\text{Al}_2\text{O}_3, \text{CeO}_2, \text{CuO}$ ) and since aluminium oxide has been calcinated at the temperature of 500°C, its mass can be regarded as stable.

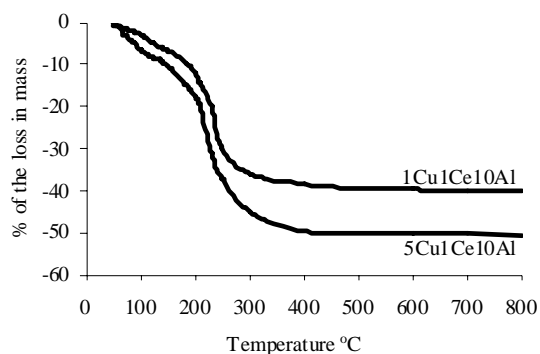


Figure 1. The percentage change of loss of mass with the calcination temperature degree for (5Cu1Ce10Al, 1Cu1Ce10Al).

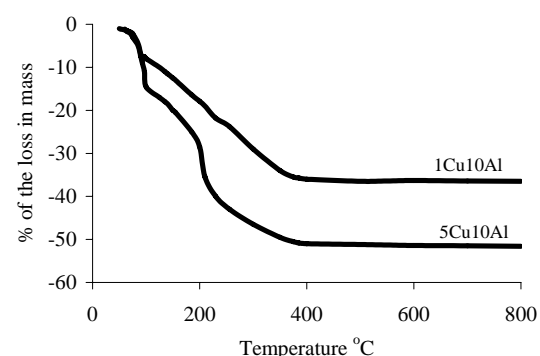


Figure 2. The percentage change of loss of mass with the calcination temperature degree for (5Cu10Al, 1Cu10Al).

We note from Table 2 that the experimental values are always higher than the theoretical values by 10 to 17%. The difference between the experimental and theoretical values equals, as shown in Figures 1 and 2, the percentage of the loss of mass at a temperature below that of 180°C.

Table 2: represents the percentage of the theoretical and the experimental loss of mass in these catalysts.

Catalysts	Theoretical loss of mass %	Experimental loss of mass %
5Cu1Ce10Al	39.12	50.8
1Cu1Ce10Al	25.6	40.2
5Cu10Al	37.3	52.6
1Cu10Al	15.49	38.2
1Cu1Ce	30	42

This loss agrees with the release of physically adsorbed water and the water of crystallization. When comparing the percentage of the theoretical loss of mass with that of the experimental loss between the temperatures 180°C and 400°C which represents the decomposition of nitrates, we note an agreement between these values. We note a slight change in the loss of mass between the temperatures 500°C and 800°C that is no more than 1%. This

emphasises the lack in mass of  $\text{Al}_2\text{O}_3$  despite it has been calcinated at temperature  $500^\circ\text{C}$ .

From Figure 1 and upon comparing the catalysts  $5\text{Cu}1\text{Ce}10\text{Al}$ ,  $1\text{Cu}1\text{Ce}10\text{Al}$ , we note that the catalyst which contains the highest percentage of copper loses physically adsorbed water, and decomposes at lower temperature degrees, because the point of the deflection of the catalysts' curve ( $5\text{Cu}1\text{Ce}10\text{Al}$ ) takes place at temperature  $225^\circ\text{C}$  and equals  $252^\circ\text{C}$  for ( $1\text{Cu}1\text{Ce}10\text{Al}$ ). Figure 2 shows that for the catalysts ( $5\text{Cu}10\text{Al}$ ,  $1\text{Cu}10\text{Al}$ ) we note the same thing, the point of juncture is about  $206^\circ\text{C}$  for the catalyst ( $5\text{Cu}10\text{Al}$ ) but it is  $230^\circ\text{C}$  for ( $1\text{Cu}10\text{Al}$ ).

We also note that the presence of cerium slightly delays the process of nitrates' decomposition because the point of deflection of the catalysts ( $5\text{Cu}10\text{Al}$ ) curve takes place at temperature  $206^\circ\text{C}$ , but for the catalyst ( $5\text{Cu}1\text{Ce}10\text{Al}$ ) the point of deflection happens at temperature  $225^\circ\text{C}$ . But as regards the catalyst  $1\text{Cu}1\text{Ce}$ , as revealed in Table 2, we calculated the loss of mass depending upon equation (2) which has to do with the decomposition of copper nitrates, because cerium nitrates have already decomposed as we have calcinated them at  $400^\circ\text{C}$ . Figure 3 shows the change of the percentage of loss with temperature, and as it is clear, this change is linear between normal temperature and  $300^\circ\text{C}$ . This is in agreement with the flow of physically adsorbed water, crystallization water and nitrates decomposition. It is about 42%. The percentage of the loss of mass resulting from the flow of physically adsorbed water and crystallization water nearly equals 12% at  $100^\circ\text{C}$ . The loss of the mass of cerium oxide is very slight mainly because the loss of mass beyond  $400^\circ\text{C}$  is about 2%.

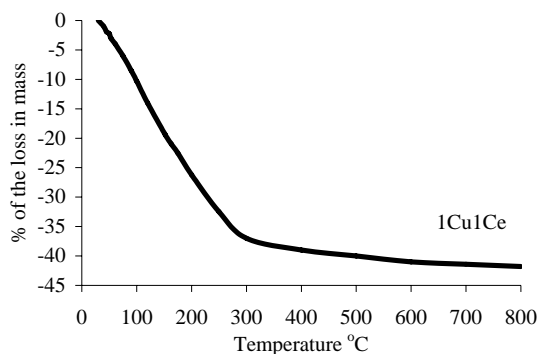


Figure 3. The percentage change of loss of mass with the calcination temperature degree for ( $1\text{Cu}1\text{Ce}$ ).

### 3.2.2. Reduction State

At first, we calcinated the specimens at  $400^\circ\text{C}$  for six hours under a current of air. Then we studied the reduction of these catalysts under a current of hydrogen. Figures 4 and 5 show the change of the percentage of the loss of mass with temperature degrees for reduction of various catalysts. The curves in these figures can be divided into three regions:

#### Region I

It is from normal temperature degree to  $110^\circ\text{C}$ . It represents the release of physically adsorbed water which comes from the humidity of the atmosphere beyond the calcinations.

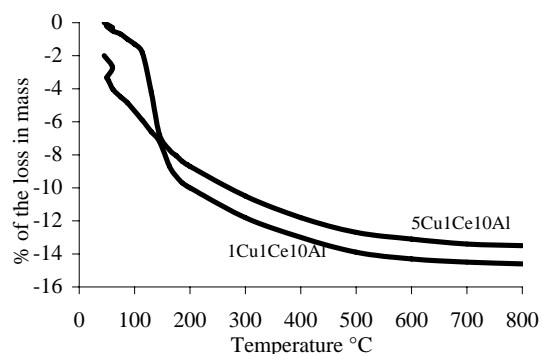


Figure 4. The change of the percentage of the loss of mass with the reduction temperature degree for  $5\text{Cu}1\text{Ce}10\text{Al}$ ,  $1\text{Cu}1\text{Ce}10\text{Al}$ .

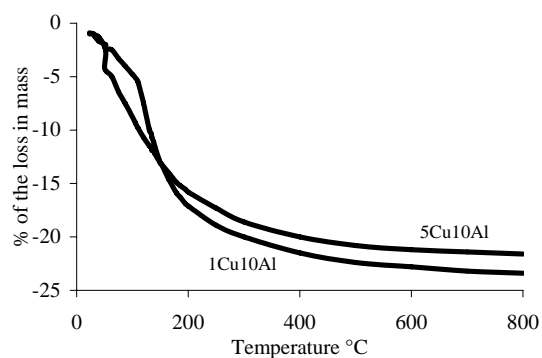


Figure 5. The change of the percentage of the loss of mass with the reduction temperature degree for  $5\text{Cu}10\text{Al}$ ,  $1\text{Cu}10\text{Al}$ .

#### Region II

It is from  $110^\circ\text{C}$  to  $190^\circ\text{C}$  in accordance with the percentage of copper oxide  $\text{CuO}$ . The theoretical loss of mass was calculated according to these equations:



#### Region III

It is from  $200^\circ\text{C}$  to  $700^\circ\text{C}$ . Here the loss of mass is continual but very slight. Table 3 shows the theoretical and the experimental values of the percentage of the loss of mass during the reduction process. When comparing the loss of mass in the reduction and oxidation, we note that the loss of mass resulting from the release of physically adsorbed water takes place more easily during reduction than during oxidation where it happens at temperatures below  $100^\circ\text{C}$ .

Table 3: Theoretical and Experimental loss of the mass during the reduction of the oxides comprising the catalyst.

catalysts	Theoretical loss in mass %		Experimental loss in mass %	
	CuO	CuO+CeO <sub>2</sub>	Region II	The loss in mass %
5CuCe10Al	7.43 %	8.13 %	110-160 °C	6.32 %
1Cu1Ce10Al	2.10 %	3.15 %	145-170 °C	1.82 %
5Cu10Al	8.82 %	8.82 %	110-160 °C	8.30 %
1Cu10Al	2.71 %	2.71 %	135-180 °C	2.17 %

We also note that the amount of the loss of mass during reduction is far less than that during oxidation. In this case the source for adsorbed water on the catalysts surface is the vapour in the atmosphere which adsorbs on the catalysts surface after the calcination process and the removal of the samples from the reactor and keeping it. But in the oxidation case there is a loss of the water of nitrates crystallization  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in addition to that of physically adsorbed water.

In Region II we note from the curves that between 110°C and 190°C the loss of mass almost equals the theoretical loss of mass for copper oxide (see Table 3). Thus the loss of mass in this region includes the reduction of copper oxide only. We also note that the temperature for reduction is low when the amount of copper is bigger in catalysts, and this seems clear in the deflection point which equals 130°C for the catalysts 5Cu1Ce10Al and 5Cu10Al, but it reaches 155°C for the catalyst 1Cu1Ce10Al, and 166°C for the catalyst 1Cu10Al. For temperatures higher than 200°C, we note a very slight and continual decrease in mass with the rise of temperature until it reaches 700°C.

In regions II and III together, namely between 110°C and 700°C we note that the experimental loss of mass is higher than the theoretical loss of mass for the reduction of CuO in catalyst 1Cu10Al and catalyst 5Cu10Al and the same thing for the oxides CeO<sub>2</sub> and CuO together in catalysts (5Cu1Ce10Al) and (1Cu1Ce10Al). It seems that Al<sub>2</sub>O<sub>3</sub> contributes a little to the loss of mass through the loss of the roots of hydroxyl on its surface. In contrast to what we noted in the curves representing the situation of oxidization under a current of air, the loss of mass has to do with the amount of nitrates impregnated on aluminium oxide. But in the situation of reduction the loss of mass for the catalysts, which do not contain cerium (5Cu10Al, 1Cu10Al), will be greater because cerium is one of the heaviest elements and it does not constitute a high percentage in the compound, and its reduction in accordance with the equation (4) only constitutes a loss of mass amounting to 4.65%, but when reducing CuO which is calculated on the basis of equation (3), the loss of mass equals 20.13% and for the catalysts void of cerium Ce, the greater loss of mass happens to the catalyst which contains a lesser amount of copper 1Cu10Al, which asserts the loss of the roots of hydroxyl from the surface of Al<sub>2</sub>O<sub>3</sub>, and this was confirmed experimentally. As for the catalyst 1Cu1Ce, the theoretical loss of mass calculated means of equation (3) equals 6.36%, through CuO does not represent more than nearly 31.6% of the catalyst.

The complete reduction of the catalyst in accordance with equations (3) and (4) leads to the loss of mass by 9.54%. Figure 6 reveals the loss of mass in catalyst

1Cu1Ce with the reduction temperature. From this figure we note that the loss of mass from normal temperature to 600°C equals 10.63%, which, besides representing the reduction process, represents the release of physically adsorbed water from normal temperature to 85°C. We also note a loss of mass which amounts to 1.35% which represents the process of the release of physically adsorbed water. Afterwards we note the sudden decrease in mass from 85°C to 110°C. This decrease can be estimated up to 5.9%. This value approximates the theoretical value calculated for reducing CuO.

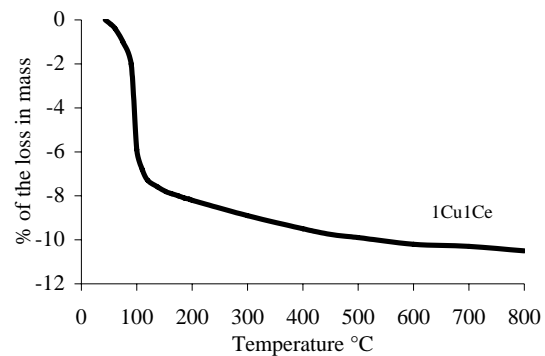


Figure 6. The change of the percentage of the loss of mass with the reduction temperature degree for 1Cu1Ce.

In comparison with the other catalysts, we note that CuO can be reduced at lower temperature when it is impregnated on cerium oxide. This phenomenon could result from the existence of the pair  $\text{Ce}^{+3}, \text{Ce}^{+4}$  and its ability to be reduced which eases the process of reduction of  $\text{Cu}^{+2}$ . From 110°C to 600°C we note a continual loss of mass until we reach a percentage of loss which can be estimated as 9.28%, a value approximating the value theoretically calculated for reducing CuO to Cu and CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub>.

#### 4. Conclusion

Impregnating copper and cerium on aluminium oxide leads to the decrease of specific surface area, and copper has the greater effect upon this change compared to cerium. Between the calcinations temperatures of 300°C and 500°C we note the presence of a slight change in the specific surface area, but beyond 500°C up to 800°C there is a great decrease in the specific surface area.

The decomposition of nitrates impregnated onto aluminium or cerium oxide under current of air takes place in temperatures ranging between 200°C and 300°C, and the nitrates decomposition has to do with the percentage and nature of the metal impregnated.

The study of the reduction of the catalysts in an atmosphere of hydrogen shows that the increase of the percentage of copper in the catalyst eases the reduction of copper oxide therein. The use of cerium oxide as a support lowers the reduction temperature degree of CuO compared with aluminium oxide Al<sub>2</sub>O<sub>3</sub>. The reason for this facility of reduction of Cu<sup>+2</sup> could be the result of the partial reduction of CeO<sub>2</sub> to form non-stoichiometric oxide CeO<sub>2-x</sub>, this partially reduced oxide can ease the electron transfer to the Cu<sup>+2</sup> to reduce it easier. Cerium oxide in the two catalysts 5Cu1Ce10Al and 1Cu1Ce10Al can also form a non-stoichiometric cerium oxide by partial hydrogenation, but the electron transfer happens between CeO<sub>2-x</sub> and the hydroxyl roots existing on the surface of aluminium oxide.

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