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Catalytic Oxidation of Carbon Black Over Ru/Co_xMg_yAl₂ CatalystsAmal Aoun^a, Samer Aouad^{a,*}, John El Nakat^a, Bilal El Khoury^a, Edmond Abi Aad^{b,c},
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Abstract

Different catalysts based on ruthenium impregnated on hydrotalcites (Ru/Co_xMg_yAl₂-HT) were prepared by wet impregnation from aqueous nitrosyl nitrate solutions and activated under air at 600°C for 4 h. The reactivity of the catalysts was evaluated in the oxidation of carbon black (CB). The results showed that the best catalyst decreased the temperature at which the rate of carbon black oxidation is the highest by about 150°C. This good reactivity was attributed to the formation of easily reducible ruthenium and cobalt oxide species at the surface of the support. The addition of ruthenium made the reduction of surface and bulk cobalt oxides possible at lower temperatures.

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Carbon Black; Catalyst; Hydrotalcites; Oxidation; Ruthenium

1. Introduction

Industrial chimneys, gasoline and diesel engines emit carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x). They also produce significant amount of particulate matter (PM) constituted mainly of soot (carbon black) and a volatile organic fraction (VOF) of hydrocarbons that have condensed on soot [1]. Soot causes serious problems to human health and environment. The best option for the removal of soot is its collection and oxidation at temperatures present in diesel cars exhausts and/or in industrial stacks. The use of a catalyst decreases significantly the temperature of carbon black oxidation [2]. The contact between soot and catalyst is a very important parameter in catalytic oxidation of soot. Only limited information is available on the intimacy of the solid-solid contact

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between the catalyst and the soot under real conditions. It can be seen that in general the mixtures with “loose contact” have a high combustion temperatures, while samples prepared with “tight contact” have low combustion temperatures [3].

Hydrotalcites (HT) are naturally occurring clay minerals that can be used in catalysts for several applications [4]. On the other hand, ruthenium oxide catalysts have been demonstrated to be reactive in acetic acid, propene and carbon black oxidation reactions. The pronounced reactivity of ruthenium oxide catalysts seems to result from the reducibility of the oxide itself [5]. Many studies showed that the structure of heterogeneous catalysts is dynamic and is intimately dependent on the reaction conditions. Such dynamic changes have been observed on Co and Ru catalysts during methanol oxidation indicating that the active state of the catalyst exists during the process of catalysis [6]. In addition, on cobalt oxide surfaces, molecules are chemisorbed at room temperature. While dissociation was observed upon annealing and in the presence of oxygen both, partial (carbon monoxide, formaldehyde) and complete oxidation product (carbon dioxide) can be produced depending on the conditions [6]. Co presents two stable bulk phases of cobalt oxide CoO and Co₃O₄. The thermodynamically stable form of cobalt oxide under ambient temperature and pressure conditions is the Co₃O₄ [6]. Alumina (Al₂O₃) is often used as a support in oxidation catalysts due to its thermal stability and significant specific surface area [7]. A few studies have been devoted to the total oxidation of carbon black (CB) over Ru/HT-like catalysts; however, literature shows that ruthenium catalysts are reactive in different oxidation reactions [8].

In this paper the catalytic oxidation of carbon black over different Ru/Co_xMg_yAl₂-HT catalysts is investigated.

2. Experimental

In order to combine many metals into one homogeneous phase, the co-precipitation at constant pH method is adopted. In this way of synthesis the structure of the formed HT is directly related to the fixed pH value [9-12]. Co-Mg-Al (HT) were prepared by precipitating ions in aqueous solution with adequate quantities of Co(NO₃)₂·4H₂O (SIGMA-ALDRICH, 98% pure), Mg(NO₃)₂·4H₂O (FLUKA, 99% pure) and Al(NO₃)₃·9H₂O (FLUKA, 98% pure) with a NaOH solution (HIMEDIA, 99% pure) and sodium carbonate solution Na₂CO₃ (HIMEDIA, 99.5% pure). Metals solution is added drop wise to an aqueous solution of sodium carbonate (pH of 10 adjusted with sodium hydroxide solution) heated to 60°C. The mixture is kept at 60°C during 2 hours while for maturation. The obtained mixture is then placed inside an oven at 60°C for 24 hours and the so obtained precipitate is filtered, washed and then dried at 60°C. Different hydrotalcites, with an atomic ratio (Co²⁺ + Mg²⁺)/Al³⁺ = 3, were synthesized. These solids are named Co₆Al₂HT, Co₄Mg₂Al₂HT, Co₂Mg₄Al₂HT, and Mg₆Al₂HT. These solids calcined at 400°C in order to obtain the stable mixed oxides before ruthenium impregnation. To prepare Ru/Mg_xCo_yAl₂-HT catalysts, an adequate volume of Ru(NO)(NO₃)_x(OH)_y solution (1.7 wt. % Ru) was added to the above calcined solids with 50 mL of water in order to obtain solids with ruthenium 1 wt.%. The obtained mixture is then stirred during 2 hours for maturation. Catalysts were thermally stabilized by calcinations at 600°C (1°C.min⁻¹) under air flow (2L.hr⁻¹) during 4 hours.

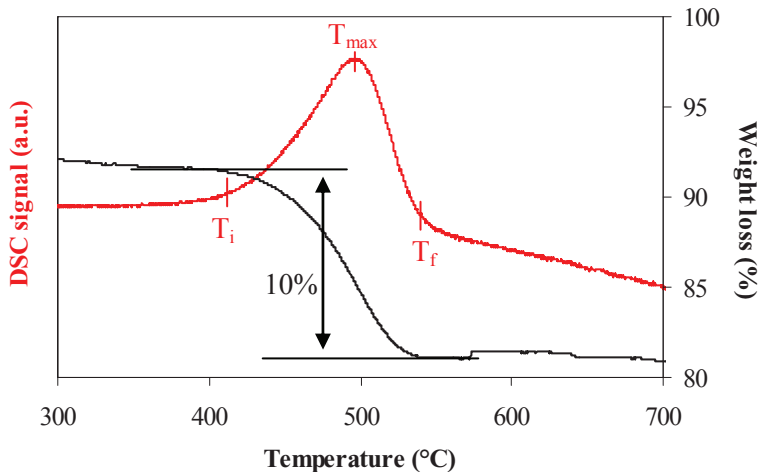
The catalytic test towards the combustion of carbon black CB¹, was studied by simultaneous thermogravimetric (TG) - differential scanning calorimetry (DSC) analysis using a Labsys Evo apparatus. Before test, 10 wt.% of CB and 90 wt.% of catalyst were mixed for 5 minutes using a mortar and a pestle. Ten milligrams of the mixture were then loaded in an alumina crucible and heated from room temperature up to 900°C (5°C.min⁻¹) under air flow of 50 mL.min⁻¹. The temperature programmed reduction (TPR) analysis was carried in situ using a U-shaped flow type reactor. Hydrogen (5 vol.% in Ar) was passed through the reactor containing the catalyst under atmospheric pressure at 30 mL.min⁻¹. The tube was heated with an electric furnace at a 5°C.min⁻¹ rate, and the amount of H₂ consumed was monitored with a thermal conductivity detector.

¹ N330 DEGUSSA: specific surface area S_{sp} = 76 m².g⁻¹, composition: 97.23 wt.% C; 0.73 wt.% H; 1.16 wt.% O; 0.19 wt.% N; 0.45 wt.% S.

3. Results and discussions

In order to establish a scale for the reactivity of the different oxides on one hand and to assure the reproducibility of the mechanical mixtures catalyst/carbon black on the other hand, the factors time of mixing and catalyst/carbon black ratio are fixed and maintained constant for all the tests. The catalyst/carbon black ratio in each mixture was 9/1 in weight and the mixture was crushed in a mortar for 10 minutes.

Figure 1 is an example of DSC/TG curves obtained during carbon black oxidation in the presence of a catalyst. For all the tests, the TG curves showed a total weight loss of ~10% corresponding to the complete combustion of carbon black mixed with the catalyst, whereas DSC curves show an exothermic peak corresponding to CB combustion.



From the DSC curve on figure 1, three temperatures are important:

- T_i : carbon black oxidation ignition temperature often called “onset temperature”.
- T_{max} : temperature at which the rate of CB oxidation is the highest
- T_f : temperature at which the oxidation is completed

Fig. 1: Example of a DSC/TG curve of “90% catalyst + 10%CB” mixture

Figure 2 shows the characteristics oxidation temperatures obtained with the different $1RuCo_xMg_yAl_2$ catalysts. It is observed that reactivity increases with the cobalt content of the catalyst. In fact, all the catalysts showed a decrease in T_{max} relatively to the uncatalyzed reaction (~630°C). This decrease ranged from 30°C to 160°C for $1RuMg_6Al_2$ and $1RuCo_6Al_2$ respectively.

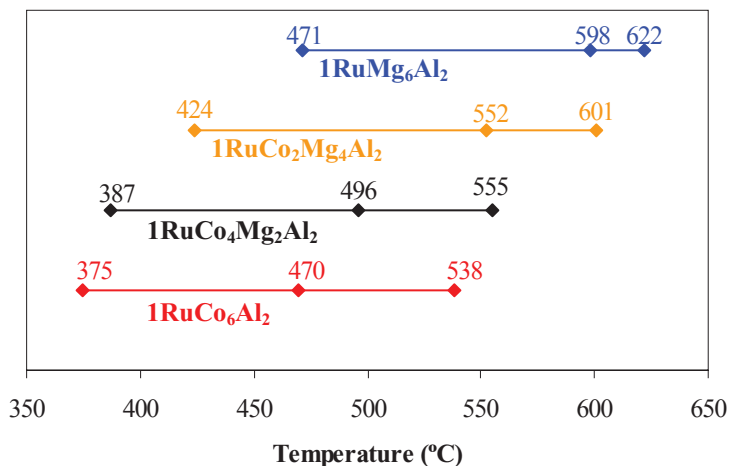


Fig. 2: Characteristic carbon black oxidation temperatures in the presence of the different catalysts

In order to understand the correlation between the increased reactivity with the cobalt content, and the effect of ruthenium addition to the supports, a temperature programmed reduction study was done on the supports calcined at 400°C and the corresponding catalysts calcined at 600°C. Figure 3 shows the hydrogen consumption for the different solids. It is observed that Mg_6Al_2 does not consume hydrogen all over the temperature range. This is not surprising as it is known that aluminum and magnesium oxide do not reduce in the considered temperature range. Once cobalt is present in the mixed oxides, two reduction peaks appear on the TPR profiles. The intensity of the peaks increases with the cobalt content, but their surfaces ratio remains constant whatever the cobalt content. According to this observation and to the literature, the two peaks are attributed to various cobalt oxide species mainly CoO and Co_3O_4 [13]. Moreover, the curves show a slight shift in the second peak toward lower reduction temperatures (from 781°C till 703°C) with increasing Co content. This is most due to kinetic considerations where an increase in reactive sites content affects the rate of the reaction making it faster at lower temperatures.

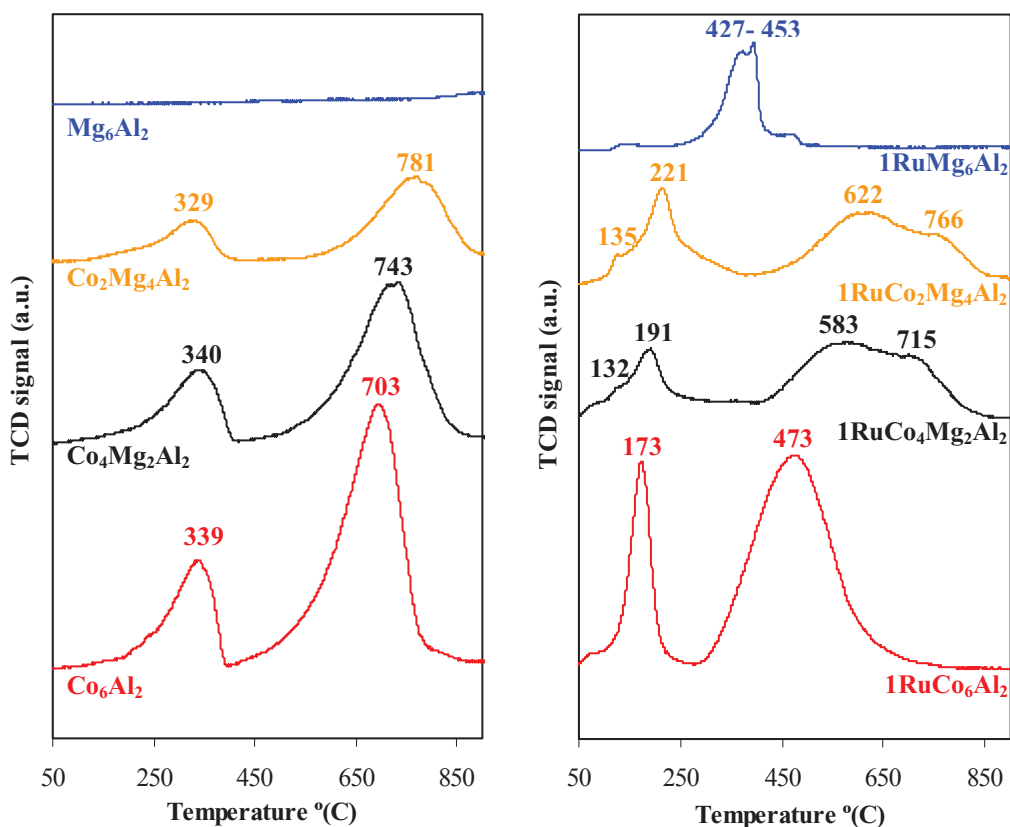


Fig. 3: TPR profiles of $Co_xMg_yAl_2HT400$ and $1RuCo_xMg_yAl_2HT600$ solids

From the literature, the partial HT reconstruction during the impregnation step permits the Ru incorporation by replacement of active site of Mg^{2+} or Al^{3+} in the HT layers [14-16] leading to a better dispersion of the active phase. The impregnation of 1 wt. % Ru on the above supports showed a dramatic change in the TPR profiles. One composite peak is observed for $1RuMg_6Al_2$. This latter is attributed to the reduction of RuO_x species with different cluster sizes. The modification of the supports with ruthenium shifted the Co oxides species reduction peaks to lower temperatures. This shift affected both reduction peaks observed for calcined supports. Moreover, this decrease is greater for higher cobalt contents showing the formation of a greater amount of easily reducible species in the presence of ruthenium. The first peak is attributed to simultaneous reduction of ruthenium and cobalt oxide species. As for carbon black oxidation, easily reducible species are required to catalyze the reaction at low temperatures, the

TPR results give a good explanation for the observed catalytic behavior on figure 1. In fact, T_{max} is the lowest for $1RuCo_6Al_2$ which presents two reduction peaks at $173^\circ C$ and $473^\circ C$. Accordingly, the nature of the reactive catalytic site is affected by the presence of ruthenium, and the interaction with cobalt oxide species leads to better catalytic reactivity in CB oxidation.

3. 4. Conclusion

In this study, $Co_xMg_yAl_2HT$ were prepared by a coprecipitation method. The thermal decomposition at $400^\circ C$ led to mixed oxides having reduction temperatures in the range of $330^\circ C$ to $780^\circ C$ (except Mg_6Al_2 /no reduction peak). The modification of the supports with 1 wt.% ruthenium shifted this temperature range to lower values. This effect was beneficial to the catalytic oxidation of carbon black. The reactivity increased with the presence of more easily reducible species. The greater amount of these reactive species was encountered with the catalyst having the highest cobalt content. As many oxidation reactions require an easily reducible catalyst, the modification of $Co_xMg_yAl_2HT$ with ruthenium is promising to achieve such goals.

Acknowledgments

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