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Carbon black and propylene oxidation over Ru/Co_xMg_yAl₂O_z catalystsSamer Aouad^{a,*}, Amal Aoun^a, Mira Skaf^{a,b,c}, Madonna Labaki^d, John El Nakat^a, Bilal El Khoury^a, Pierre Obeid^a, Edmond Abi-Aad^{b,c}, Antoine Aboukais^{b,c}^a Department of Chemistry, Faculty of Sciences, University of Balamand, P.O. Box 100, Deir El Balamand, Kelhat, Tripoli, Lebanon^b University Lille Nord de France, 59000 Lille, France^c ULCO, LCE, 59000 Dunkerque, France^d Laboratory of Physical Chemistry of Materials, Faculty of sciences II, Lebanese University, PO Box 90656, Fanar, Lebanon

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ABSTRACT

The effects of Co_xMg_yAl₂O_z mixed oxides composition and ruthenium addition on the oxidation of propylene and carbon black (CB) were investigated. Different reactive cobalt and ruthenium oxide species were formed following calcination at 600 °C. The addition of ruthenium was beneficial for the CB oxidation under “loose contact” conditions and for propylene oxidation when the cobalt content was intermediate to low. The calculated activation energy for CB oxidation was decreased from 151 kJ mol⁻¹ for the uncatalyzed reaction to 111 kJ mol⁻¹ over the best catalyst.

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R É S U M É

Les effets de la composition des oxydes mixtes Co_xMg_yAl₂O_z ainsi que leur dopage par du ruthénium sur l'oxydation catalytique du noir de carbone et du propène ont été étudiés. La calcination des solides à 600 °C a contribué à la formation de différentes espèces réactives de cobalt et de ruthénium. L'addition de ruthénium s'est avérée bénéfique pour l'oxydation du noir de carbone sous les conditions de « contact faible » ainsi que pour l'oxydation de propène lorsque la teneur du solide en cobalt est relativement faible. L'énergie d'activation pour l'oxydation du noir de carbone est passée de 151 kJ mol⁻¹ en absence de catalyseur à 111 kJ mol⁻¹ en présence du solide le plus performant.

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1. Introduction

Industrial chimneys, gasoline and diesel engines emit considerable amounts of particulate matter (PM) as well as volatile organic compounds (VOC) [1]. One of the principal solutions to reduce their emissions is the catalytic oxidation technique [2,3]. Several mixed oxides systems

presenting high oxygen storage capacity were investigated for their use in catalytic oxidation reactions [4–6]. However, these latter are relatively costly and they may present some environmental adverse effects. Cobalt, magnesium and aluminium mixed oxides synthesized by hydrotalcite route (HT) and used as supports for different metals are potential candidates to deal with cost and toxicity problems. They were tested in several catalytic reactions as the oxidation of carbon black (CB) [7] and VOC [8]. Moreover, supported precious metals such as Pt and Pd are well established as efficient catalysts for VOCs combustion [9] but unfortunately are very expensive and are susceptible to poisoning. On the other hand, ruthenium oxide based catalysts are cheaper and have showed good reactivity in acetic acid, propene and CO

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oxidation reactions and in various catalytic reactions such as: water-gas shift, ammonia synthesis and reduction of NO [2,10]. Indeed, the association of ruthenium oxide and ceria establishes a successful catalytic system in oxidation reactions [11,12]. In fact, under oxidative conditions, Ru is transformed to RuO₂, showing highly desirable reactivity and stability and having a lower cost than other noble metals. However, few if any studies have been devoted to the total oxidation of volatile organic compounds and carbon black in the presence of ruthenium supported on cobalt, magnesium and aluminium mixed oxides.

In this study, Ru/Co_xMg_yAl₂O_z solids were developed and their reactivity was evaluated in CB and propylene oxidation reactions in order to consider their use as a potential solution for some types of air pollution emissions.

2. Experimental

Four different Co_xMg_yAl₂O_z mixed oxides supports (*x* and *y* are the numbers of cobalt and magnesium atoms respectively in one formula unit) with an atomic ratio (Co²⁺ + Mg²⁺)/Al³⁺ = 3 were prepared and stabilized as detailed in [7]. An adequate quantity of Ru(NO)(NO₃)₃ solution (1.7 wt.% Ru) was added to 1 g of the calcined supports already dispersed in 50 mL of water to obtain a nominal metallic Ru content of 1 wt.% in the final catalyst. The obtained mixture is then stirred during 2 h for maturation, and left overnight to dry in the oven at 60 °C. Catalysts were thermally stabilized by calcination at 600 °C (1 °C min⁻¹) under air flow (2 L h⁻¹) during 4 h.

X-ray diffraction (XRD) experiments were performed at ambient temperature on a Bruker D8 Advance diffractometer using Cu Kα radiation (1.5405 Å). The diffraction patterns were indexed by comparison with the JCPDS files. Temperature programmed reduction (TPR) was carried out on a ZETON ALTAMIRA apparatus. Hydrogen (5 vol.% in Ar) was passed through a U-shaped reaction tube containing the catalyst under atmospheric pressure at 30 mL min⁻¹. The tube was heated with an electric furnace at 5 °C min⁻¹, and the amount of H₂ consumed is monitored with a thermal conductivity detector.

The oxidation of carbon black CB (N330 Degussa: S_{sp} = 76 m² g⁻¹, elementary analysis: 97.23 wt.% C; 0.73 wt.% H; 1.16 wt.% O; 0.19 wt.% N; 0.45 wt.% S), 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 manually shaken for 5 min inside a plastic tube to obtain “loose contact” conditions (L) or grinded for 10 min using a mortar and a pestle to obtain “tight contact” conditions (T). An amount of 10 mg 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. Propylene (C₃H₆ 6000 ppm) oxidation was carried out in a U-shaped catalytic fixed bed micro-reactor (diameter: 1 cm/catalytic bed height: 2 mm), coupled to a Varian 3600 gas chromatograph using a double flame ionization and thermal conductivity detection. An amount of 100 mg of a catalyst were used with a total gas flow (air + propylene) of 100 mL min⁻¹ and a heating rate of 1 °C min⁻¹.

3. Results and discussion

3.1. XRD characterization

XRD patterns of freshly calcined Ru/Co_xMg_yAl₂O_z catalysts are shown in Fig. 1. The Ru/Mg₆Al₂O_z catalyst pattern presents diffraction lines corresponding to the MgO periclase phase (JCPDS N°45-0946) and the MgAl₂O₄ mixed oxides phase (JCPDS N°73-1959). Moreover, diffraction lines characteristic of RuO₂ in a tetragonal phase (JCPDS N°40-1290) are observed on the same pattern. For cobalt-containing catalysts, the patterns present diffraction lines corresponding to Co₃O₄ (JCPDS N°42-1467), CoAl₂O₄ (JCPDS N°44-0160) and Co₂AlO₄ (JCPDS N°38-0814) crystallized in a spinel phase. It is not possible to distinguish between these different mixed oxides using the XRD technique since they give similar patterns. It is important to note that despite the presence of the same ruthenium amount, the diffraction lines corresponding to RuO₂ became less intense for the Ru/Co₂Mg₄Al₂O_z catalyst and totally disappeared for higher cobalt contents. This result shows that ruthenium oxide species tend to form well-crystallized agglomerates when magnesium content is high. On the other hand, the presence of cobalt enhances the dispersion or ruthenium oxide species or even facilitates the incorporation of some ruthenium atoms into the spinel phase described above.

3.2. Catalytic results

Fig. 2 shows the parameter T_{50%} that represents the temperature at which 50% of carbon black or propylene is converted in the presence of Co_xMg_yAl₂O_z supports or Ru/Co_xMg_yAl₂O_z catalysts. It is observed that Co_xMg_yAl₂O_z supports do not show significant catalytic reactivity in the CB oxidation test under “loose contact” conditions.

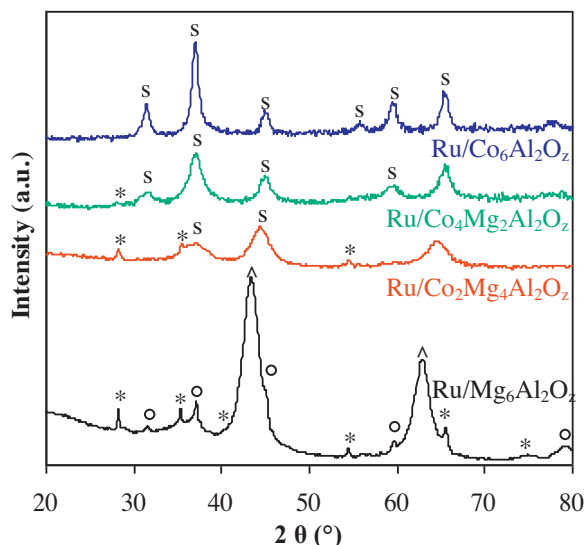


Fig. 1. XRD patterns for Ru/Co_xMg_yAl₂O_z catalysts. “s”: Co₃O₄ (JCPDS N°42-1467), CoAl₂O₄ (JCPDS N°44-0160) and Co₂AlO₄ (JCPDS N°38-0814) mixed oxides; “*”: RuO₂ phase (JCPDS 40-1290); “^”: MgO periclase phase (JCPDS N°45-0946); MgAl₂O₄ mixed oxides (JCPDS N°73-1959).

However, the Ru/Co_xMg_yAl₂O_z catalysts decreased $T_{50\%}$ under the same contact conditions. For example, a substantial 70 °C decrease from 629 °C (without any catalyst) down to 559 °C for Ru/Co₆Al₂O_z was observed. This can be explained by a “spill over” mechanism of O₂ over Ru oxide species. In fact the dissociative adsorption of oxygen over metallic ruthenium is low ($\approx 10^{-6}$), but when a very small quantity of RuO₂ is formed on the surface, the reaction of oxide formation is self catalyzed because the dissociative adsorption coefficient of oxygen over ruthenium oxide is high (0.7) [13]. Moreover, in loose contact, the mobility of ruthenium oxide species plays a major role knowing that the Tamman temperature of RuO₂ is close to the observed temperature range in the carbon black oxidation under “loose contact”. In addition, a decrease of $T_{50\%}$ is observed when the amount of cobalt is increased. Under “tight contact” conditions, it is clearly observed that all prepared solids are significantly reactive in the total oxidation of CB and that $T_{50\%}$ are much lower than those obtained for “loose contact” conditions. This is due to the grinding that decreased the aggregates sizes, increasing the number of contact points between catalytic sites and CB. Moreover, it appears that ruthenium addition did not contribute significantly to the catalytic reactivity under “tight contact” conditions. In fact, the grinding leads to several direct contact points between cobalt oxide species and carbon particulates, which makes the oxidation of these latter possible at lower temperatures and making the promoting effect of ruthenium less important. Thus, the presence of ruthenium can be considered as a precursor for the initiation of CB oxidation at low temperature and for “loose contact” conditions. Once the reaction is initiated, cobalt oxides take over to complete the redox cycle. In order to evaluate the contribution of the best catalyst (Ru/Co₆Al₂O_z), the activation energy (E_a) and the Arrhenius

parameter (A) were calculated based on the method described in [14]. In this method, the required data are directly retrieved from TG curves and used in the below equation:

$$\ln\left(\frac{-\Delta m}{\Delta t} m^{-n}\right) = \ln A - \frac{E_a}{RT}$$

where m is the actual mass of the sample undergoing reaction, Δm the mass variation during the time interval Δt , R the perfect gas constant, T the absolute temperature and n an adjustment parameter. The assumption of $n = 1$ is made for this analysis according to [14]. Computed E_a and $\ln A$ values are reported in Table 1. The activation energy for the non-catalyzed reaction (Al₂O₃ used for dilution as it is inert in the considered reaction [15]) is in line with values already reported in the literature for the combustion of carbonaceous materials [16]. The presence of ruthenium decreased the same value to around 138 kJ mol⁻¹ under “loose contact” conditions. This is a substantial decrease keeping in mind that the fraction of molecules with enough energy to undergo efficient collisions and lead to products is an exponential function. For the “tight contact” mixture, the activation energy is even lower for reasons that were stated above.

Concerning propylene oxidation, it is to be noted that total conversion is not achieved before 690 °C [12]. The support that showed the best reactivity in total propylene oxidation is Co₆Al₂O_z with a $T_{50\%} = 182$ °C (Fig. 2) compared to ~ 550 °C for the non-catalyzed reaction [12]. Compared to the other supports, Mg₆Al₂O_z presents the lowest reactivity. For supports with high cobalt contents, ($x = 4$ and $x = 6$), the addition of ruthenium did not significantly enhance the catalytic reactivity. However, for lower cobalt contents ($x = 2$ and $x = 0$), ruthenium addition contributed to lower $T_{50\%}$ (Fig. 2). This can be explained by the fact that the weight percentage of ruthenium is small compared to that of cobalt for high x values and therefore its contribution is negligible compared to that of cobalt. While, for low x values, the catalytic reactivity of ruthenium oxides becomes important compared to less reactive cobalt oxide species (on an atom to atom basis) and therefore $T_{50\%}$ values were decreased. It is worth mentioning that the selectivities towards CO and CO₂ were monitored in both CB and propylene oxidation reactions and were found to be equal to 0% and 100%, respectively, whatever the catalyst used.

The catalytic behavior of the different solids may be partially explained by the XRD results presented at the beginning of this section. In fact, catalysts with high cobalt content showed the best reactivity owing to the good dispersion of ruthenium oxide species, which initiate the different reactions. However, the contribution of the

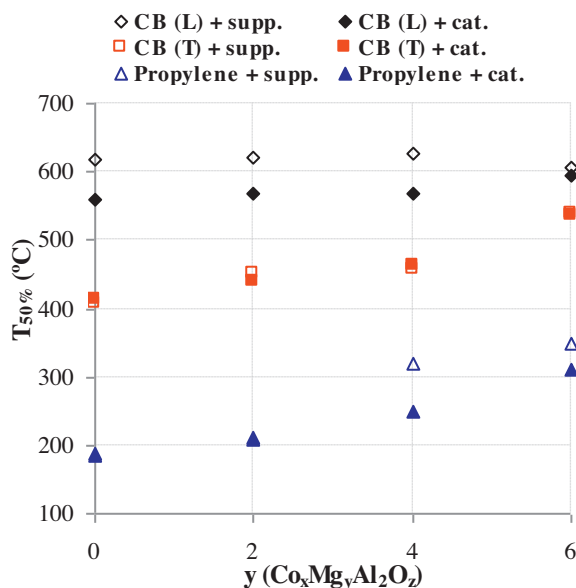


Fig. 2. Effect of the support composition on $T_{50\%}$ for the carbon black and propylene oxidation reactions over Co_xMg_yAl₂O_z and Ru/Co_xMg_yAl₂O_z solids.

Table 1

Activation energies and Arrhenius pre-exponential factor for the non-catalyzed and catalyzed CB oxidation.

Reaction	E_a (kJ mol ⁻¹)	$\ln A$
Al ₂ O ₃ + CB	151	18.5
Ru/Co ₆ Al ₂ + CB (L)	138	17.3
Ru/Co ₆ Al ₂ + CB (T)	111	17

support composition to the catalytic reactivity is difficult to elaborate using the XRD results.

3.3. TPR Results

In order to gain more insight in the catalytic process-taking place during the reactions, a TPR study was done on the different calcined solids. Fig. 3 shows TPR profiles of calcined $\text{Co}_x\text{Mg}_y\text{Al}_2\text{O}_z$ supports and $\text{Ru}/\text{Co}_x\text{Mg}_y\text{Al}_2\text{O}_z$ catalysts. $\text{Mg}_6\text{Al}_2\text{O}_z$ does not show any reduction peak due to the non-reducibility of magnesium oxides species in the studied temperature range. Cobalt containing supports present two reduction peaks. The first peak (I) is situated in the 270 °C to 370 °C range while the second peak (II) appears in the 600 °C to 850 °C range. These two peaks are attributed to the reduction of Co_3O_4 and Co–Al mixed oxides species, respectively. The area of those peaks increases with the increase of Co content. The maximum temperature of peak II is shifted towards lower temperatures when the amount of cobalt increases due to kinetic considerations that suggest that the reduction temperature decreases when the amount of reactive sites increases. The $\text{Ru}/\text{Mg}_6\text{Al}_2\text{O}_z$ solid showed one composite reduction peak attributed to the reduction of RuO_x species with different cluster sizes. Cobalt-containing catalysts showed two reduction peaks. The first peak (I) in the 150 °C to 230 °C temperature range is attributed to simultaneous reduction of ruthenium and cobalt oxide species. The second peak (II) in the 280 °C to 420 °C temperature range corresponds to the reduction of Co–Al mixed oxides species that behave similarly to CoAl_2O_4 spinel [17] that will be reduced into $\text{Co}(0)$. The modification of the supports with ruthenium shifted the Co oxides species reduction peaks to lower temperatures. This shift affected both reduction peaks, (I) and (II), observed for calcined

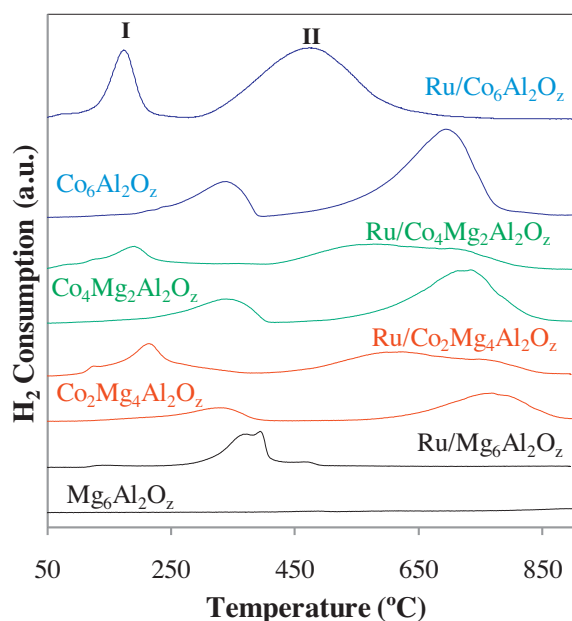


Fig. 3. H_2 -TPR profiles for the different $\text{Co}_x\text{Mg}_y\text{Al}_2\text{O}_z$ supports and $\text{Ru}/\text{Co}_x\text{Mg}_y\text{Al}_2\text{O}_z$ catalysts.

supports. 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 TPR results make it clear that the oxidation reduction behavior of the solids is responsible for the catalytic reactivity in the oxidation reactions. In fact, for higher cobalt contents, more easily reducible species are present and participate in the catalytic process. The addition of ruthenium made the reduction of those species possible at even lower temperatures, which allowed the earlier initiation of the oxidation reactions.

4. Conclusion

$\text{Co}_x\text{Mg}_y\text{Al}_2\text{O}_z$ mixed oxides are cheap and reactive in carbon black (tight contact) and propylene oxidation reactions. However, under real conditions, the contact between soot and the catalyst is more represented by the “loose contact” mixing. To promote the reactivity of these supports under “loose contact” conditions, the addition of a small amount of ruthenium (1 wt.%) can be considered. The presence of ruthenium oxide species initiates the oxidation reaction at lower temperatures especially when cobalt content is low.

Disclosure of interest

The authors declare that they have no conflicts of interest concerning this article.

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