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ScienceDirect
Catalysis Today 119 (2007) 273–277
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Reactivity of Ru-based catalysts in the oxidation of propene and carbon black

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Available online 26 September 2006

Abstract

The relationship between the state of Ru on different supports and catalytic activity in the oxidation of propene and carbon black was investigated for catalysts prepared by different impregnation methods. It is demonstrated that the addition of ruthenium to ceria (CeO_2), alumina (Al_2O_3) and ceria–alumina significantly improves the reactivity: the temperature of carbon black oxidation decreases by 100–140 °C. It is also shown that the addition of Ru to the different supports is very beneficial for the total oxidation of propene. Temperature programmed reduction (TPR) experiments of the catalysts showed that the oxygen species of ruthenium oxides are reduced at low temperatures which is the main reason of its high reactivity in oxidation reactions.

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Keywords: Ruthenium; CeO_2; Al_2O_3; Oxidation; Carbon black; Propene; TPR

1. Introduction

The harmful effect of particulates (diesel emissions and industrial effluents), and volatile organic compounds (VOCs) on human health has become a subject of great concern, and has resulted in the restrictive legislation both in the EU and the US [1–5]. These emissions may pose significant health risks [6] and play an important role in atmospheric chemistry as precursors of secondary pollutants [7].

To meet current emission standards for vehicles and industrial effluents, efficient catalytic converters for the complete oxidation of hydrocarbons (HC) and soot particles are required. It was shown that under practical conditions, the activity of catalysts for soot oxidation is low. Therefore, it was concluded that under practical conditions the contact between soot and catalyst is poor [8].

A few studies have been devoted to the total oxidation of volatile organic compounds (VOCs) and carbon black (CB) over Ru/Al_2O_3 and Ru/CeO_2. However, literature data shows that ruthenium oxide catalysts are active in acetic acid [9] and propene oxidation [10] reactions.

In this work, we describe the activity of ruthenium catalysts towards the oxidation of propene and carbon black (CB) particulates. The contact used for catalysts and CB mixtures is denoted ‘‘loose contact’’ and is representative of contact conditions existing in diesel exhausts and industrial effluents. Catalysts containing various amounts of ruthenium were prepared and its catalytic activity has been investigated.

2. Experimental

2.1. Solids preparation

Two kinds of Ru/CeO_2 catalysts were prepared:

(1) Cerium hydroxide $Ce(OH)_4$ was prepared by precipitation from cerium(III) nitrate hexahydrated solution $Ce(NO_3)_3\cdot 6H_2O$ 0.25 M with an alkali solution NaOH 1 M. The resulting hydroxide $Ce(OH)_4$ was filtered, washed and dried overnight in a drying oven at 100 °C, then it was calcined at 500 °C to obtain ceria CeO_2. Different volumes of ruthenium(III) nitrosyl nitrate $Ru(NO)(NO_3)_3$ solution have been impregnated on ceria in order to obtain solids with different loadings of ruthenium (0.67, 1, 3, 5 wt.%). These solids have been designated as Ru_xCe (x stands for the Ru wt.%). After drying at 100 °C for about 20 h, solids

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doi:10.1016/j.cattod.2006.08.030

were stabilized by calcination under dried air at 600 °C for 4 h.

(2) For the other catalysts $Ru_xCe(A)$, cerium hydroxide was precipitated from 500 mL of 6.0×10^{-2} M cerium(III) nitrate aqueous solution at pH of about 11 by adding 3 M NaOH followed by stirring for 30 min. After the precipitate was filtered, it was again dispersed in 500 mL of deionized water. A known amount of $RuCl_3$ and formaldehyde (HCHO/Ru = 5 M ratio) were added to the dispersion, and the mixed solution was stirred at 90 °C for 1 h. Then, 3 M NaOH was added to the mixed solution until the pH of the solution was about 11. The solid portion was filtered and washed with deionized water until the pH of the filtrate was below 9. The solid was dried at 80 °C overnight followed by calcination at 600 °C for 4 h in air.

Alumina (Al_2O_3) is synthesized by sol–gel method [11]. Secondary aluminium butylate is dissolved in butan-2-ol at 85 °C. Then, complexing agent butan-1,3-diol preliminary heated at 60 °C is added before hydrolysis. Hydrolysis is performed by addition of water to the solution at 85 °C. The gel is dried and calcined under oxygen flow at 500 °C for 4 h. The Ru_xAl catalysts with different ruthenium contents were prepared by the same method as for the Ru_xCe catalysts (1). To prepare Ru_xnCe10Al catalysts (x = Ru wt.%, n number of Ce atoms for 10 Al atoms), $Ce(NO_3)_3$ aqueous solution was first added (porous volume) to previously prepared Al_2O_3 support, then the mixture was dried overnight, calcined at 500 °C for 4 h, followed by impregnation of Ru as indicated in method (1).

2.2. Experimental conditions

The catalytic test towards the combustion of CB N330 (DEGUSSA) was studied by simultaneous TG-DTA analysis with NETZSCH STA 409 apparatus. Before test, 20 wt.% of CB and 80 wt.% of catalyst were mixed slightly in an appropriate cell for 10 min: ‘‘loose contact’’. Thirty milligrams of this mixture were loaded in an alumina crucible and heated from room temperature up to 1000 °C (5° C min^{-1}) under air flow of 75 mL min^{-1}. The propene (C_3H_6) oxidation was realized in a catalytic micro reactor coupled to a Varian 3600 gas chromatograph using a double detection FID and TCD. The catalysts were reactivated at 500 °C for 1 h under a flow of dried air 35 mL min^{-1}. Hundred milligrams of the catalyst were tested in the presence of propene (air + propene = 100 mL min^{-1}; 6000 ppm of propene).

2.3. TPR analysis

Temperature programmed reduction (TPR) was carried out with a flow type reactor. Hydrogen (5 vol.% in Ar) was passed through a 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 H_2 consumed was monitored with a TC detector.

2.4. TPO analysis

Temperature programmed oxidation (TPO) was carried out with a flow type reactor. Oxygen (10 vol.% in He) was passed through a 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 O_2 consumed was monitored with a TC detector.

3. Results and discussion

Taking in consideration the volatility of ruthenium oxides at high temperatures, a thermogravimetric study of Ru_xCe solids was performed to elucidate all doubts about its use for carbon particles and VOCs combustion. Fig. 1 shows TG curves of non-calcined Ru_1Ce catalyst heated from room temperature up to 600, 700 and 800 °C (5 °C min^{-1}) under air flow of 75 mL min^{-1} followed by a 4 h isotherm at the final temperature. For each sample, a weight loss of about 3.2% is observed up to 550 °C. This loss corresponds to the departure of physically adsorbed water and the decomposition of nitrates and nitrosyls groupings coming from the precursor $Ru(NO)(NO_3)_3$. For the samples heated at 600 and 700 °C, no other weight loss is observed during the isotherms, and the total weight loss is about 3.2%. The curve at 800 °C shows a different layout, especially at ~730 °C, where a new weight loss is observed (about 0.3% after 4 h at 800 °C). This result was confirmed by a temperature programmed oxidation study of a calcined Ru_1Ce catalyst. Fig. 2 shows that oxygen consumption for the calcined sample begins at ~730 °C, which is in correlation with the TG study. In fact, at these temperatures, RuO_2 is oxidized and forms RuO_4 which is highly volatile with boiling point of 40 °C [12] and this results in Ru loss. As the highest temperature used for our oxidations is largely lower than 730 °C, the use of our solids is possible for the catalytic oxidation of carbon particles and VOCs. However, a local temperature increase could be envisaged during the catalytic oxidation and may cause Ru loss. For that, an elementary analysis was led on samples before and after tests, and it showed that there was no Ru loss even after 10 cycles of carbon black and propene oxidation.

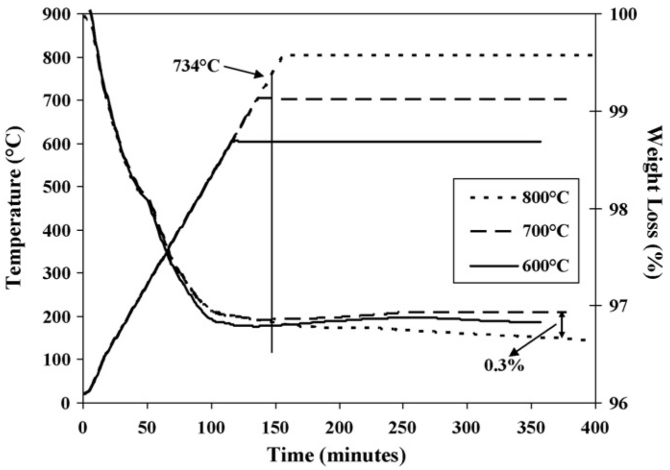

Fig. 1. TG profiles of non-calcined Ru_1Ce catalyst.

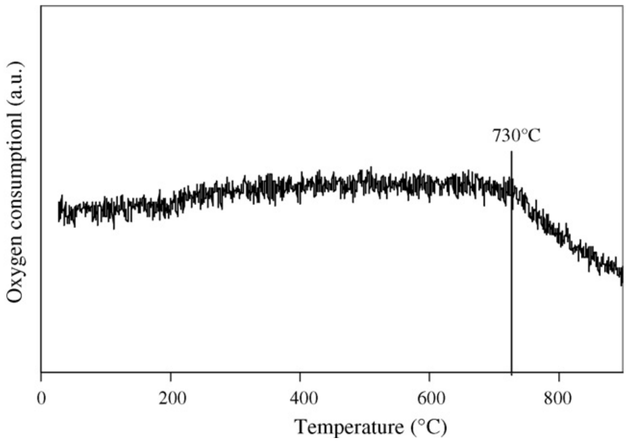

Fig. 2. TPO profile of Ru_1Ce catalyst calcined at 600 °C.

Table 1 shows T_{max}, temperature of the maximum of the DTA-curve that corresponds to the temperature of the highest rate of CB combustion. Catalytic properties of solids are evaluated by comparing these temperatures with those of CB combustion without catalyst in the same conditions. The total combustion of CB without any catalyst was performed using SiC as an inactive support and has exhibited only one exothermic peak with a maximum of combustion temperature at about 629 °C. When the combustion was performed in the presence of ceria, a decrease of about 17 °C of the CB T_{max} value was observed. Thus, even if ceria was shown as a very active catalyst in the CB combustion in ‘‘tight contact’’ mixtures [13], it appears that it does not favour this same reaction under ‘‘loose contact’’ conditions. However, in the presence of ruthenium, a decrease of about 100–140 °C of the temperatures values was observed showing that the presence of this metal oxide enables carbon black combustion at lower temperatures (490–530 °C). It is also observed that the T_{max} for CB combustion is lower for Ru_xCe and $Ru_xCe(A)$ catalysts (∼490 °C) than for Ru_xAl catalysts (∼530 °C). This is probably related to the mobility of oxygen species on catalyst surface. It appears that the presence of ruthenium oxides on ceria increases this mobility more significantly compared to its presence on alumina. This could be explained by the study of the reducibility of these different solids. In an earlier work, it was observed that Ru is present as ruthenium oxide (RuO_2) on solids surface after calcination at 600 °C [14]. Table 2 represents reduction temperatures (T_R) corresponding to ruthenium oxide RuO_2 for the different catalysts. It is observed that RuO_2 reduction for the Ru_xAl catalysts occurs at higher temperatures than those corresponding to Ru_xCe which can explain the better reactivity of these latter mentioned in carbon black oxidation. Nevertheless, the catalytic reactivity is stable for ruthenium loading ≥1% as T_{max} remains unchanged at about 490 °C despite the increase of Ru loading from 1% to 5%. This could be caused by a saturation of ceria surface by ruthenium oxides ($x\%/1 < x < 3$) causing the formation of clusters in poor interaction with the support. In fact, it is observed (Table 2) that $Ru_{0.67}Ce$ and Ru_1Ce present one reduction peak, whereas Ru_3Ce and Ru_5Ce present two distinguished peaks. These latter indicates the presence of different ruthenium oxide species on ceria surface and probably the formation of agglomerates of this oxide which are more difficult to reduce than the well dispersed ruthenium oxide species reduced at low temperatures (∼65 °C). Thus, it is concluded that a 1% Ru loading is sufficient to reach the optimal reactivity of the catalysts.

Table 1
Catalytic activity performance in CB oxidation expressed in terms of T_{max} (the temperature corresponding to the maximum reaction velocity) of various ruthenium-based catalysts

Mixtures	T_{max} (°C)
SiC + CB	629
CeO_2 + CB	612
$Ru_{0.67}Ce$ + CB	506
Ru_1Ce + CB	492
Ru_2Ce + CB	490
Ru_3Ce + CB	493
Ru_5Ce + CB	490
$Ru_1Ce(A)$ + CB	514
$Ru_3Ce(A)$ + CB	488
$Ru_5Ce(A)$ + CB	489
Al_2O_3 + CB	624
Ru_1Al + CB	528
Ru_3Al + CB	531
Ru_5Al + CB	526
1Ce10Al + CB	587
$Ru_1$1Ce10Al + CB	528
$Ru_3$1Ce10Al + CB	529
$Ru_5$1Ce10Al + CB	527
3Ce10Al + CB	578
$Ru_1$3Ce10Al + CB	517
$Ru_3$3Ce10Al + CB	522
$Ru_5$3Ce10Al + CB	520
5Ce10Al + CB	581
$Ru_1$5Ce10Al + CB	487
$Ru_3$5Ce10Al + CB	490
$Ru_5$5Ce10Al + CB	494

$RuO_2/CeO_2–Al_2O_3$ catalysts are prepared and their reactivity is evaluated to study the synergetic effects between ceria and alumina. It is observed that for these catalysts a lower activity than Ru_xCe catalysts is obtained during the carbon black oxidation. It seems that Ru_x1Ce10Al catalysts are equally reactive as Ru_xAl catalysts, with $T_{max} \sim 530$ °C, whereas Ru_x5Ce10Al catalysts present the same reactivity as Ru_xCe and $Ru_xCe(A)$ with $T_{max} \sim 490$ °C. Thus, a better interaction between ruthenium and ceria is envisaged when the latter's content is increased. Furthermore, this increase helped the

Table 2
Reduction temperature of Ru_xCe and Ru_xAl catalysts

	T_R (°C)		
Ru_xCe			
$Ru_{0.67}Ce$		66	
Ru_1Ce		65	
Ru_3Ce	68		128
Ru_5Ce	68		135
Ru_xAl			
Ru_1Al	102		134
Ru_3Al	113		163
Ru_5Al	115		154

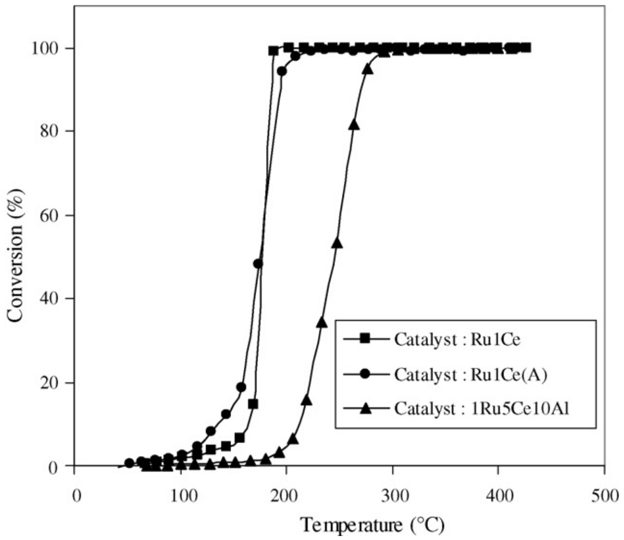

Fig. 3. Propene conversion vs. reaction temperature on different Ru(1 wt.%)-based catalysts.

oxygen in the gas to be adsorbed on the surface [15]. This adsorbed oxygen is the most active oxygen species, therefore, the activity of Ru_xnCe10Al catalysts is higher than that of Ru_xAl catalysts in CB oxidation.

The behaviour of the most reactive oxides in carbon black oxidation is studied for the propene oxidation. Fig. 3 shows the catalytic activity with respect to the oxidation reaction of propene in the presence of Ru_1Ce, Ru_1Ce(A) and $Ru_1$5Ce10Al. It is observed that the total conversion of propene occurred for all the catalysts at temperatures lower than 300 °C. It should be mentioned that propene conversion did not exceed 22% over alumina [16] and 62% over ceria at 400 °C [13]. It is also known that total conversion of propene alone occurs at about 600 °C and the 50% conversion at about 500 °C. The catalytic performance of the ruthenium-based catalysts is presented in Fig. 4 in terms of the temperature ($T_{50\%}$) needed to reach 50% C_3H_6 conversion. For Ru_xCe and Ru_xCe(A) catalysts $T_{50\%} \sim 175$–185 °C which is nearly 320 °C less than $T_{50\%}$ for propene alone (500 °C). However, for Ru_x5Ce10Al catalysts, a lower activity in propene oxidation is observed with $T_{50\%} \sim 230$ °C. In fact, as mentioned before, with the increase of ceria content in the catalysts, interactions between adsorbed oxygen species and C_3H_6 are more efficient and this latter is totally eliminated at lower temperatures.

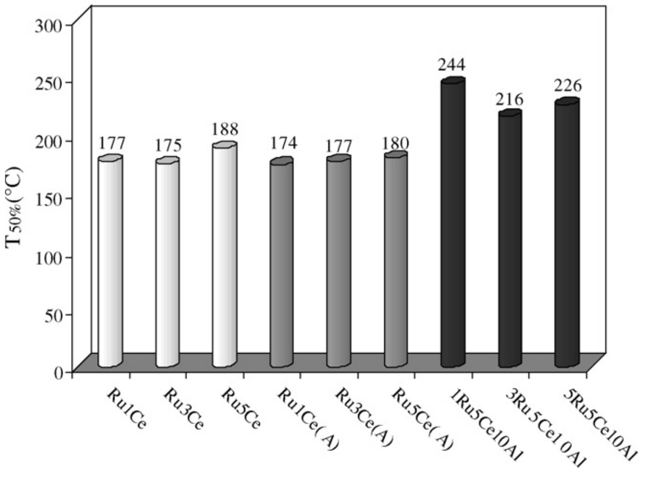

Fig. 4. Catalytic activity performance in propene oxidation expressed in terms of $T_{50\%}$ (the temperature needed to reach 50% propene conversion) of various Ru-based catalysts.

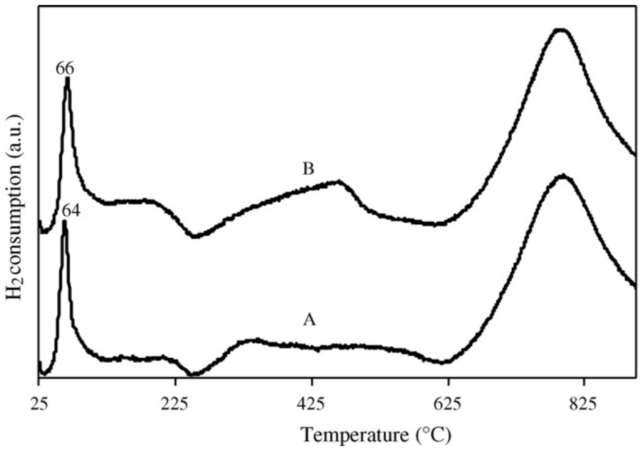

Fig. 5. TPR profiles of Ru_1Ce catalyst: ''freshly calcined'' (A) and ''after carbon black test'' (B).

Since the ruthenium loading >1% did not affect the reactivity of the solids, and after analysing the TPR results we can probably conclude that Ru–Ce–O bonds in the well-dispersed Ru species are highly fragile and its mobile oxygen are active for the carbon black and propene oxidation. Even if oxygen belonging to these Ru compounds is consumed during oxidation and the state of Ru becomes metallic, atmospheric oxygen is readily incorporated into solid and Ru will be in an oxidized state again. To confirm this hypothesis, a TPR study was done on an already used sample for carbon black combustion. Fig. 5 shows that the TPR profiles obtained for the ''used'' sample (B) and for the ''fresh'' (non-used) sample (A) are practically similar before 200 °C and that oxygen is reincorporated at low temperatures in the catalyst. However, an increase in hydrogen consumption at about 450 °C is observed. This phenomenon clearly shows that ceria can be partially reduced during ruthenium oxide reduction. Indeed, partial reduction of ceria has been observed in presence of precious metal [17] and non-precious metal [18] by a spillover process. This consumption became more important after several cycles. This can be explained by a hydrogen spillover phenomenon which apparently is favoured by the formation of a new ruthenium species on ceria surface after carbon black oxidation.

4. Conclusions

In conclusion, the Ru-supported catalysts are active in the combustion of propene and carbon black. Even in the case of a ''loose contact'', these doped ruthenium catalysts allowed the combustion of the carbon black at temperatures close to 490 °C, largely lower than those obtained with ceria (612 °C) under practical conditions. This reactivity is due to the weakness of the Ru–O–Ce bonds, which allows the mobility of oxygen, an easy reduction of RuO_2 at low temperatures and thus the complete oxidation of carbon black at temperatures close to those present in diesel exhaust line and even in industrial chimneys. Moreover, the reactivity of catalysts increases with the ruthenium content until a content of 1%. Indeed, for this quantity of ruthenium, there is ruthenium oxide saturation on ceria surface confirmed by TPR results, which explains a stabilization of catalysts reactivity from 1% out of ruthenium. These catalysts were shown also very active in the oxidation of propene with a $T_{50\%} \sim 175\ ^\circ C$ for the best catalysts.

These results are very promising for the use of these catalysts in the struggle to control the carbonaceous particles and volatile organic compounds pollution.

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