Catalysis Today 176 (2011) 120–125

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

VOCs removal in the presence of NO_x on Cs–Cu/ZrO_2 catalysts

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ARTICLE INFO

Article history:
Received 30 September 2010
Received in revised form 10 January 2011
Accepted 24 January 2011
Available online 18 February 2011

Keywords:
Cs
Cu
ZrO_2
Oxidation catalyst
VOCs
NO_x

ABSTRACT

The effect of Cs and Cu on the physicochemical characteristics of zirconium oxide and the catalytic properties of the corresponding solids in the oxidation of toluene are studied. The influence of NO_x as oxidizing agent is also investigated. Cu(II) species in Cs_x–Cu_y/ZrO_2 catalysts correspond to dispersed Cu(II) and CuO crystallites in interaction with the alkali promoter. The low activity of Cs_x–Cu_y/ZrO_2 with high amount of Cs is explained by the low specific area and to the presence of CuO crystallites. Moreover, NO_x are strongly adsorbed in the form of nitrate species in Cs_x–Cu_y/ZrO_2 with high amount of Cs, hindering the toluene conversion. Cs_x–Cu_y/ZrO_2 catalysts with low Cs content are highly active in toluene oxidation and NO_x acts in this case as an oxidizing agent. Dispersed Cu(II) species in interaction with Cs are both responsible of the catalytic activity and the transformation of NO into NO_2 prior to the oxidation of toluene.

1. Introduction

Combustion processes generally produce different pollutants, as particulate matter, sulphur oxides (SO_x), nitrogen oxides (NO_x) and volatile organic compounds (VOCs). In order to reduce atmospheric emissions from sources such as biomass and waste incinerators, catalytic devices appear as an efficient technology available for complete oxidation of VOCs or/and NO_x reduction. During the last two decades, transition metal oxides have gained much interest for their ability to act as active phase in supported catalysts either for VOCs oxidation [1,2] and NO_x reduction [3]. In addition, some studies showed the possibility to produce simultaneously VOCs oxidation and NO_x reduction [4,5].

Among active transition metal oxides, supported Cu(II) systems have been widely investigated [6–10]. Their activity highly depends on copper dispersion and both acidic and redox properties of the Cu(II) phase make such catalysts interesting for oxidation as well as reduction reactions.

Up to now, relatively few works have been devoted to CuO/ZrO_2 for application in these reactions [8,9,11–13]. Cu(II) deposited on ZrO_2 surface lead to the formation of dispersed species easily reducible and responsible of the performance of such systems. Moreover, the use of low amounts of alkali in catalysts was shown to enhance oxidative properties in hydrocarbons oxidation [14].

The aim of this work was to evaluate the catalytic behaviour of Cs_x–Cu_y/ZrO_2 catalysts in the oxidation of toluene and study the effect of NO_x as oxidizing agent in the flue gas. The preparation of Cs_x–Cu_y/ZrO_2 was performed considering different Cs/Zr (0.015 and 0.15) and Cu/Zr (0.1 and 0.2) molar ratios. To correlate the catalytic properties of Cs_x–Cu_y/ZrO_2 systems with their physicochemical features, information on solids were provided from the application of TG–DTA, XRD, FTIR and TPR techniques.

2. Experimental

ZrO_2 support was prepared by a precipitation method [15]. After drying at 115 °C for 24 h, this solid was calcined under air flow (2 L h^{-1}) at 300 °C for 4 h. Cs–Cu/ZrO_2 solids were then prepared by impregnation or co-impregnation of Cs_2CO_3 and/or $CuCO_3 \cdot n Cu(OH)_2$ salts onto ZrO_2. After drying, the samples were calcined under air flow at 600 °C for 4 h. The as-obtained solids were denoted Cs_x–Cu_y/ZrO_2, where x (0.015 or 0.15) and y (0.1 or 0.2) correspond to Cs/Zr and Cu/Zr atomic ratios respectively. The chemical composition of the samples was determined by ICP-MS with a Varian 820 MS apparatus. TG–DTA experiments were performed on a Netzsch STA 409 apparatus in air (75 mL min^{-1}, 5 °C min^{-1}). BET surface areas were measured by nitrogen adsorption at 77 K on a Qsurf M1 apparatus (Thermo Electron Corporation). XRD measurements were performed on a Bruker D8 Advance diffractometer using CuK_α radiation (λ = 1.5406 Å). TPR measurements were achieved with a Zeton Altamira AMI 200 apparatus

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doi:10.1016/j.cattod.2011.01.033

Table 1
Chemical composition, BET surface areas and H_2-consumption values for Cs_x–Cu_y/ZrO_2 samples.

Catalyst	Molar ratios		BET surface area	H_2-consumption ($\mu mol/g_{catalyst}$)	
	Cs/Zr	Cu/Zr	($m^2\ g^{-1}$)	Theoretical consumption	Experimental consumption
ZrO_2	–	–	84	–	–
$Cs_{0.15}/ZrO_2$	0.15	–	21	–	473
$Cs_{0.15}$–$Cu_{0.1}/ZrO_2$	0.12	0.09	12	597	942
$Cs_{0.015}$–$Cu_{0.1}/ZrO_2$	0.013	0.10	96	788	641
$Cu_{0.1}/ZrO_2$	–	0.09	90	701	710
$Cs_{0.15}$–$Cu_{0.2}/ZrO_2$	0.12	0.17	17	1088	1343
$Cs_{0.015}$–$Cu_{0.2}/ZrO_2$	0.016	0.19	93	1387	1060
$Cu_{0.2}/ZrO_2$	–	0.16	112	1166	1012

as described in [16]. FTIR experiments were recorded on a Bruker Equinox 55 FTIR spectrometer with pellets diluted in KBr. Toluene oxidation was carried out in a continuous flow reactor (1000 ppm toluene and 10% O_2/N_2, total flow rate: 100 mL min^{-1}) coupled with a CP-4900 μGC (Varian) following temperature programmed reaction conditions (1 °C min^{-1}, from 200 to 500 °C). Before each activity test, the catalyst (100 mg) was dried in air (33 mL min^{-1}, 1 °C min^{-1}) at 500 °C for 4 h. The effect of the presence of NO_x (900 ppm of NO in N_2) was also studied and reaction products (NO_x, NO, NO_2, CO and CO_2) were analyzed with Xentra 4900C analyzer (Servomex). The volume hourly space velocity (VHSV), calculated at ambient temperature and atmospheric pressure, is 105,000 h^{-1}. Since catalytic tests were always carried out in the same reaction conditions (same toluene and/or NO_x flow and catalyst weight), the conversion values, which are directly comparable, were given.

3. Results and discussion

Table 1 gathers chemical composition data and specific surface areas of Cs_x–Cu_y/ZrO_2 samples. The Cs/Zr and Cu/Zr molar ratios in the catalysts are almost confirmed by chemical analysis. Indeed, the experimental Cs/Zr molar ratio is found to be close to the theoretical one when the alkali metal is impregnated alone. In the case of co-impregnation with Cu, the Cs/Zr molar ratio is 0.12 when $x = 0.15$ and varies between 0.013 and 0.016 when $x = 0.015$. The Cu/Zr molar ratio is between 0.09 and 0.1 when $y = 0.1$ and between 0.16 and 0.19 when $y = 0.2$. The observed deficits can occur during the different steps of the preparation (impregnation and/or calcination). The presence of high amount of Cs leads to a strong decrease of surface areas. On the contrary, relatively high surface areas are obtained for Cu_y/ZrO_2 and $Cs_{0.015}$–Cu_y/ZrO_2 samples.

TG–DTA curves of dried solids (Fig. 1) show that a broad exothermic peak is detected between 500 °C and 640 °C. It can be ascribed to tetragonal ZrO_2 crystallisation. This exothermic peak is typically observed around 430 °C for pure ZrO_2 [11,14,17]. Thus, the presence of Cu or Cs induces a crystallisation delay, which is content-dependent. Moreover, it is enhanced in the case of co-impregnation of Cs and Cu in comparison with samples impregnated by Cs or Cu on ZrO_2. Cu and Cs have then cumulative effects delaying the tetragonal ZrO_2 crystallisation.

The diffractograms concerning XRD study of Cs_x–Cu_y/ZrO_2 catalysts calcined at 600 °C were displayed in Fig. 2. There is a stabilization of tetragonal ZrO_2 phase (JCPDS 50.1089) with all Cs_x–Cu_y/ZrO_2 and Cu_y/ZrO_2 catalysts and the monoclinic ZrO_2

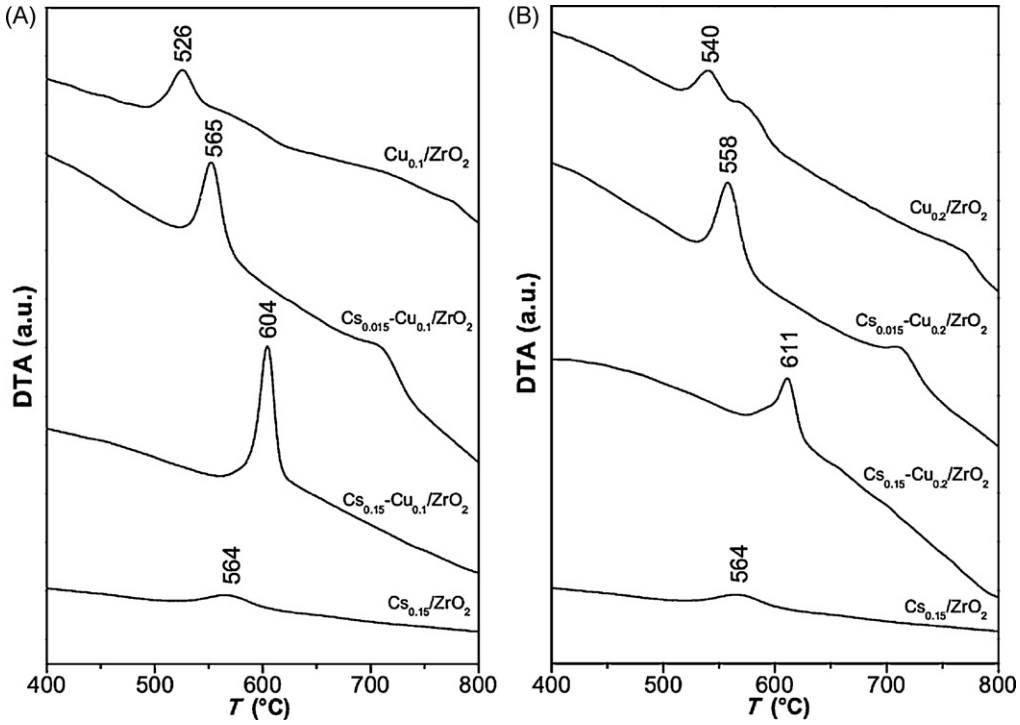

Fig. 1. DTA curves for dried Cs_x–Cu_y/ZrO_2 solids (A) Cs_x–$Cu_{0.1}/ZrO_2$ and (B) Cs_x–$Cu_{0.2}/ZrO_2$.

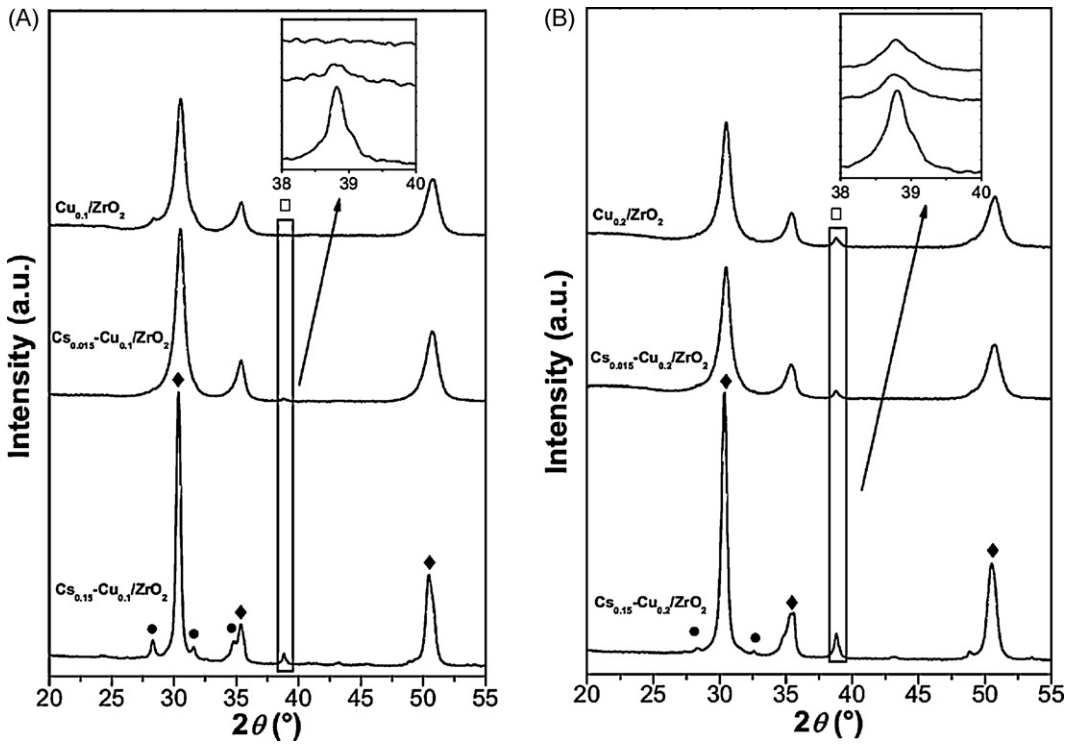

Fig. 2. XRD patterns of Cs_x–Cu_yZrO_2 calcined at 600 °C (A) Cs_x–$Cu_{0.1}/ZrO_2$ and (B) Cs_x–$Cu_{0.2}/ZrO_2$: (●) monoclinic ZrO_2 phase, (♦) tetragonal ZrO_2 phase, (□) CuO phase.

phase (JCPDS 65.1023) is significantly detected only in the case of $Cs_{0.15}$–Cu_y/ZrO_2 solids. CuO lines at $2\theta = 38.8°$ (JCPDS 48.1484) are observed in the presence of high amount of alkali metal. The same phenomenon was observed by Lick et al. [18]. The presence of alkali metal influences the Cu segregation leading to observable CuO phase with the XRD technique. These observations can be partly linked to the results of BET surface areas (Table 1), which are lower in the presence of high amount of Cs. It can be due to the important coverage of Cs species on ZrO_2 surface [19] but also to a Cs–Cu interaction leading to the Cu segregation.

TPR profile for $Cs_{0.15}/ZrO_2$ (Fig. 3) shows a first peak attributed to carbonates which have not been decomposed during calcina-

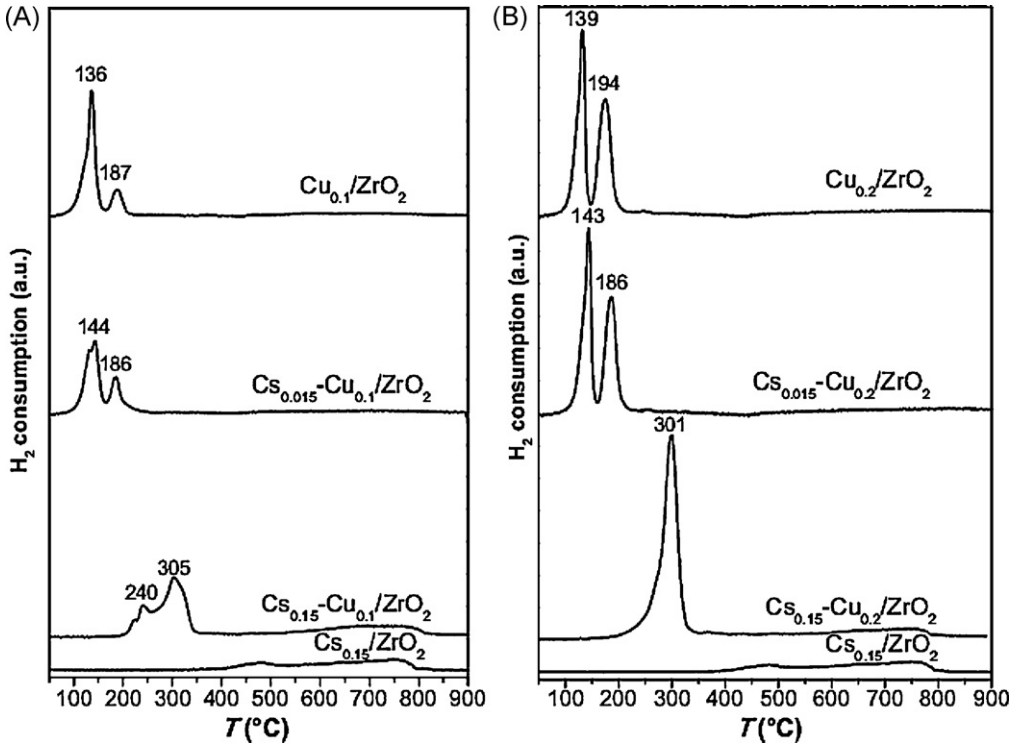

Fig. 3. TPR profiles of Cs_x–Cu_yZrO_2 calcined at 600 °C (A) Cs_x–$Cu_{0.1}/ZrO_2$ and (B) Cs_x–$Cu_{0.2}/ZrO_2$.

Table 2
Temperature at which 50% of toluene is oxidized (T_{50}) and NO_x conversion values.

Catalyst	T_{50} (°C)		NO_x conversion (%)		
	Without NO_x	With NO_x	NO_2 max. formation without toluene	NO_2 formation at the same temperature with toluene	NO_x max. conversion with toluene
$Cs_{0.15}/ZrO_2$	443	490	24.9 at 490 °C	5.7 at 490 °C	14.9 at 430 °C
$Cs_{0.15}$–$Cu_{0.1}/ZrO_2$	487	495	39.0 at 434 °C	5.7 at 434 °C	Unquantifiable
$Cs_{0.015}$–$Cu_{0.1}/ZrO_2$	260	265	47.0 at 393 °C	21.2 at 393 °C	50.0 at 280 °C
$Cu_{0.1}/ZrO_2$	266	273	59.0 at 370 °C	21.4 at 370 °C	46.4 at 282 °C
$Cs_{0.15}$–$Cu_{0.2}/ZrO_2$	424	485	50.0 at 385 °C	16.3 at 385 °C	Unquantifiable
$Cs_{0.015}$–$Cu_{0.2}/ZrO_2$	263	263	56.9 at 381 °C	17.2 at 381 °C	50.2 at 276 °C
$Cu_{0.2}/ZrO_2$	271	275	49.3 at 395 °C	15.0 at 390 °C	47.5 at 290 °C

tion (confirmed by IR characterization not shown). An additional H_2-consumption was observed at high temperature and can be attributed to the reduction of ZrO_2 which is favoured by alkali metal presence. For Cs_x–Cu_y/ZrO_2 catalysts, TPR peaks can be ascribed to the reduction of copper species, which gives two peaks between 100 and 350 °C. According to different authors [20–22], the peak at lower temperature corresponds to highly dispersed Cu(II) species and the second one to CuO aggregates. More precisely, XRD showed the formation of a higher proportion of CuO when Cs content is higher. In parallel, the second TPR peak is relatively higher following the Cu content and in the presence of Cs. These observations permit to confirm the assignment of the second peak to CuO particles. In some cases, the reduction of CuO occurs at a temperature close 350 °C in H_2-TPR experiments; however, the small size of the particle and/or the interaction of Cu(II) species with the carrier surface may explain their reduction at low temperature [23,24]. In the presence of high amount of Cs ($Cs_{0.15}$–Cu_y/ZrO_2), the TPR peaks are shifted towards higher temperature. Therefore, alkali strongly affects the reduction behaviour of copper species probably by the formation of Cs–Cu species. For the H_2-consumption during the reduction of the catalysts (Table 1), it closely corresponds to copper oxide reduction in the case of Cu_y/ZrO_2. For $Cs_{0.15}$–Cu_y/ZrO_2 solids, H_2 consumption exceeds the expected value for Cu(II) reduction. This phenomenon can be explained considering that Cs favours the reduction of ZrO_2 carrier species.

Data relative to the ability of Cs_x–Cu_y/ZrO_2 catalysts to oxidize toluene are given in Table 2. $Cs_{0.15}/ZrO_2$ and $Cs_{0.15}$–Cu_y/ZrO_2 catalysts tested without NO_x show T_{50} values between 424 °C and 487 °C. Cu-impregnation or co-impregnation of Cu and Cs on ZrO_2 leads to more active solids for $Cs_{0.015}$–Cu_y/ZrO_2, due to the presence of dispersed Cu(II) species (Figs. 2 and 3). In the presence of higher amounts of Cs, the decrease in catalytic activity can be ascribed to both the low specific area and the presence of Cu(II) species mainly in the form CuO crystallites in the corresponding solids. In the presence of NO_x, toluene conversion occurs at higher temperature in the case of catalysts with a high Cs content. This phenomenon could be due to the strong adsorption of NO_x species on the catalyst surface; leading to the formation of nitrates [12]. Indeed, FTIR measurements on tested $Cs_{0.15}/ZrO_2$ and $Cs_{0.15}$–$Cu_{0.1}/ZrO_2$ catalysts carried out after oxidation of toluene in the presence of NO_x (Fig. 4) shows a band at 1335–1355 cm^{-1} corresponding to monodentate NO_3^- [15]. The amount of nitrates is relatively larger for $Cs_{0.15}/ZrO_2$ catalyst and lower for $Cs_{0.15}$–$Cu_{0.1}/ZrO_2$. No significant adsorption was encountered for $Cs_{0.015}$–$Cu_{0.1}/ZrO_2$ and $Cu_{0.1}/ZrO_2$ samples. The large amount of nitrates adsorbed in the case of high Cs content catalysts is due to the strong basicity of Cs [14,25]. Therefore, NO_x could be stored as nitrate species on catalysts with higher alkali content. This phenomenon is in good agreement with previous works revealing the strong interaction of NO_3^- over alkali containing catalysts [15]. In our case, active oxidation sites of toluene could be occupied by NO_x explaining therefore the lower performance of the catalysts with high amount of Cs. On the contrary, whatever the test conditions (with or without NO_x) similar activities towards toluene oxidation are obtained for $Cs_{0.015}Cu_y/ZrO_2$ catalysts with lower amount of Cs. In parallel, higher NO_x conversion rates (50% between 275 and 280 °C) are obtained for $Cs_{0.015}Cu_y/ZrO_2$ compared to Cu_y/ZrO_2 catalysts. Comparing the curves of the outlet concentration of NO_x in the absence of toluene (Fig. 5(A)) and in the presence of toluene (Fig. 5(B)) for $Cs_{0.015}$–$Cu_{0.1}/ZrO_2$, the NO_x conversion maximum is observed simultaneously with the light-off of toluene oxidation. This conversion is accompanied with a decrease of NO_2 concentration (curve a). Thus, it is proposed that NO_2 participates to the oxidation of toluene and acts as an intermediate for the catalyst to work efficiently [26]. The presence of Cu and the decrease of Cs amount lead to the formation of higher proportion of NO_2 (Table 2 and Fig. 5), which has higher oxidizing property than O_2 for toluene oxidation [14]. The catalysts $Cs_{0.015}$–Cu_y/ZrO_2 possess the combination of NO_x-oxidation activity and moderate basicity, yielding to significant synergism in the oxidative adsorption on the surface. This explains the better NO_x conversion in the case of these catalysts, compared to $Cs_{0.15}/ZrO_2$ or Cu_y/ZrO_2. The oxidation of toluene is very efficient in the presence of NO_x over $Cs_{0.015}$–$Cu_{0.1}/ZrO_2$ and increasing Cu content in solids ($y = 2$) does not improve the catalytic properties for toluene oxidation.

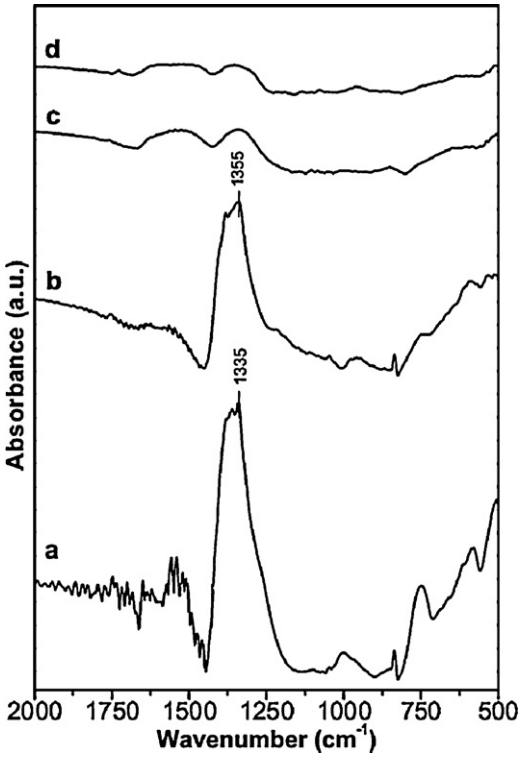

Fig. 4. Infrared spectra of the catalysts after test: toluene + NO_x: (a) $Cs_{0.15}/ZrO_2$, (b) $Cs_{0.15}$–$Cu_{0.1}/ZrO_2$, (c) $Cs_{0.015}$–$Cu_{0.1}/ZrO_2$ and (d) $Cu_{0.1}/ZrO_2$.

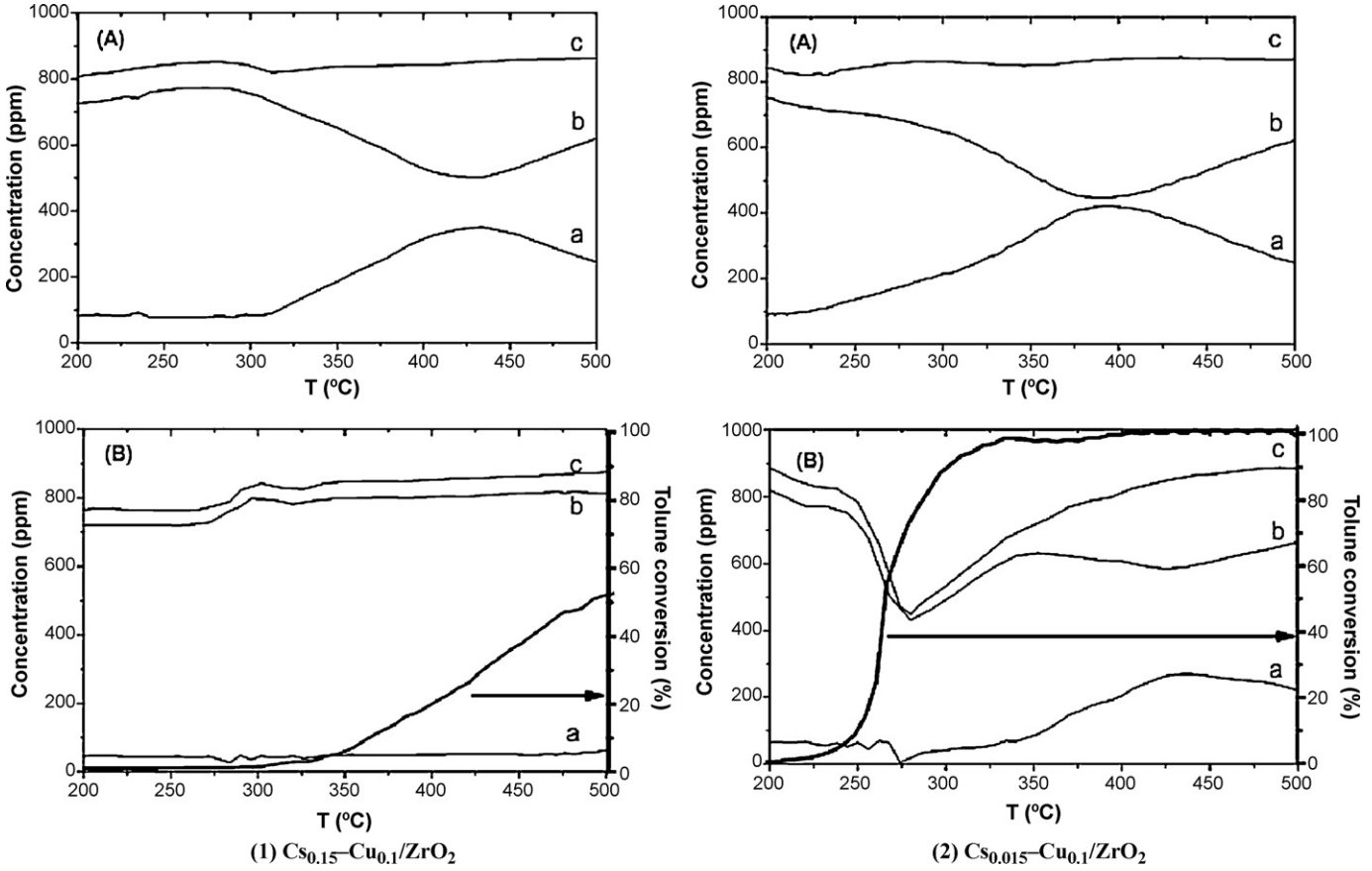

Fig. 5. Toluene conversion and outlet concentration of NO and NO_2 for $Cs_{0.15}$–$Cu_{0.1}/ZrO_2$ and $Cs_{0.015}$–$Cu_{0.1}/ZrO_2$ catalysts: (A) blank test without toluene, (B) oxidation of toluene in presence of NO_x (a: NO_2, b: NO and c: NO_x).

4. Conclusion

The catalytic oxidation of toluene in the presence of NO_x has been investigated considering cesium–copper containing ZrO_2 systems. The following characteristics of Cs_x–Cu_y/ZrO_2 solids have been evidenced:

- The presence of Cu and Cs stabilizes the tetragonal phase of ZrO_2.
- Cu(II) species supported on ZrO_2 are in the form of dispersed Cu(II) species and CuO crystallites.
- A high amount of Cs in solids favours the segregation of Cu(II) to form CuO and induces a strong decrease in catalysts specific area.

The oxidation of toluene is very efficient over $Cs_{0.015}$–Cu_y/ZrO_2 catalysts and NO_x act in this case as an oxidizing agent. The activity is related to the presence of Cu(II) dispersed species in interaction with Cs. Such systems also possess the combination of NO_x-oxidation activity and moderate basicity. However, the presence of a high amount of Cs is a drawback since a decrease in catalytic activity is encountered. This fact is explained by the low specific area and the high proportion of CuO crystallites in corresponding systems. The effect of NO_x as oxidizing agent is observed over $Cs_{0.015}$–Cu_y/ZrO_2 and NO is converted into NO_2 prior to toluene oxidation. The lower performance of the catalysts with high amount of Cs for toluene oxidation in the presence of NO_x is linked to the formation of NO_3^- species on the surface of the samples.

Acknowledgments

The "Nord-Pas de Calais" Region, the "Syndicat Mixte de la Côte d'Opale", IRENI and European Union via Interreg IV "Redugaz" project are gratefully acknowledged for financial supports.

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