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STUDY OF THE TEMPERATURE-PROGRAMMED OXIDATIVE DEGRADATION OF HYDROCARBONS OVER Ce-BASED CATALYSTS BY EVOLVED GAS ANALYSIS

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The catalytic behaviour of ceria, zirconia and ceria–zirconia mixed oxides in the temperature-programmed degradation of toluene and *n*-hexane was analysed by means of evolved gas analysis (mass spectrometry). Pure cerium oxide resulted the most active catalyst in the oxidation of both compounds. This fact revealed the crucial role of the surface oxygen species in the decomposition of this type of hydrocarbons. The low affinity of CeO_2 for H_2O and CO_2, the major oxidation products, may be also responsible for the observed highly active catalytic behaviour.

Keywords: *ceria–zirconia mixed oxides, evolved gas analysis, n-hexane, temperature-programmed oxidative degradation, toluene*

Introduction

The emission of volatile organic compounds (VOCs) has received particular attention as they have been recognised as major contributors to air pollution [1]. Catalytic oxidation is a promising strategy to reduce these emissions efficiently. Ceria-based materials as catalysts have recently attracted great interest for a wide range of practical applications due to the redox chemistry of cerium and the high affinity of the element for oxygen [2]. Undoubtedly their major commercial applications are in the treatment of emissions from internal combustion engines [3]. Nevertheless, less consideration has been given to examining the performance of this type of catalysts in the combustion of aliphatic (*n*-hexane, HEX) and aromatic (toluene, TOL) hydrocarbons, which are claimed among the most common VOCs found in industrial flue gases. The scope of this study was to analyse the catalytic behaviour of these materials in the temperature-programmed VOC oxidation by means of evolved gas analysis (mass spectrometry). Furthermore, an attempt was made to correlate the observed performance with their catalytic properties, which were evaluated by a wide range of analytical techniques.

Experimental

CeO_2 and $Ce_xZr_{1-x}O_2$ (x=0.15; 0.5; 0.68 and 0.8) were provided by Rhône-Poulenc and prepared using a coprecipitation route from nitrate precursors whereas ZrO_2 was supplied from Norton. The samples were stabilised by calcination at 550°C in air for 4 h, and then pelleted using a hydraulic press ($2.2\cdot10^4$ N cm^{-2}). Finally, pellets were crushed and sieved to obtain 0.3–0.5 mm diameter grains [4].

The textural properties were determined by N_2 adsorption-desorption at –196°C in a Micromeritics ASAP 2010 equipment. The samples were previously evacuated overnight at 300°C under high vacuum. X-ray diffraction studies were carried out on an X'PERT-MPD diffractometer with CuK_α radiation (λ=1.5406 Å) and Ni filter. A comparison of the results from XRD analysis with the reference data (CeO_2 PDF-89-8435, $Ce_{0.75}Zr_{0.25}O_2$ PDF-28-0271, $Ce_{0.6}Zr_{0.4}O_2$ PDF-38-1439, $Ce_{0.5}Zr_{0.5}O_2$ PDF-38-1436, $Ce_{0.16}Zr_{0.84}O_2$ PDF-38-1437 and ZrO_2 PDF-89-9066) helped in verifying the crystalline structure for the different oxides. Temperature-programmed desorption of various probe molecules (NH_3, H_2O and CO_2) was performed on a Micromeritics AutoChem 2910 instrument. Prior to adsorption experiments, the samples were first pre-treated at 550°C in a 5% O_2/He stream. The adsorption step was performed by either pulses of 10% NH_3/Ar, bubbling a nitrogen flow into a flask containing deionised water or a flowing 85% CO_2/Ar stream. The desorption step was carried out from 100 to 550°C at a heating rate of 10°C min^{-1} in a He stream. The desorbed gases were analysed by a thermal conductivity detector (TCD). Temperature-programmed reduction experiments were conducted on a Micromeritics AutoChem 2910 instrument as well. Samples were pre-treated in an oxygen stream at

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550°C for 1 h. Next, a gas stream of hydrogen (5% H_2/Ar) was flowed, raising the temperature from room 30 to 950°C (10°C min^{-1}). The H_2 consumption was monitored using a thermal conductivity detector. Oxygen storage capacity (OSC) measurements were carried out on a Micromeritics ASAP 2010 equipment. The sample was subjected to a reduction treatment with a pure hydrogen stream at 550°C. Finally, the oxygen consumption was recorded at 400°C. Further details on analytical procedures are given elsewhere [5].

Catalyst behaviour was examined using a lab-scale fixed-bed reactor, where the feed stream (1000 ppm of HEX or TOL) was prepared by delivering each liquid hydrocarbon by a syringe pump into dry air. A total flow rate of 500 cm^3 min^{-1} was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 30000 h^{-1}. The feed stream (1000 ppm of HEX or TOL) was prepared by delivering each liquid hydrocarbon by a syringe pump into dry air. The pumping rate of the syringe pump was previously adjusted for each hydrocarbon in order to obtain the desired concentration. The point of liquid injection was electrically heated in order to ensure complete evaporation of the reactant. Catalytic activity was measured over the range 200–550°C. The feed and effluent streams were analysed using an on-line gas chromatograph.

Additionally, the temperature-programmed decomposition of previously adsorbed HEX and TOL was investigated. The effluent stream was analysed by a TCD coupled to a mass spectrometer (HAL Quadropole Mass Spectrometer, Hyden Analytical). The experiments were conducted on a Micromeritics AutoChem 2910 instrument. Prior to HEX or TOL adsorption, the sample was pre-treated at 550°C with a stream of 5% O_2/He for 1 h. The sample was saturated with a helium stream that previously was bubbled into a flask containing liquid HEX or TOL at room temperature. The decomposition of both hydrocarbons was studied at a heating ramp of 10°C min^{-1} with flowing helium.

Results and discussion

Table 1 summarizes the main physico-chemical properties of the investigated catalysts. All cerium-containing samples showed a surface area of about 100 m^2 g^{-1} except for the $Ce_{0.15}Zr_{0.85}O_2$ sample (86 m^2 g^{-1}). The structural properties appeared to depend on the cerium content. Thus, samples with a molar cerium content higher than 68% exhibited a cubic structure whereas a tetragonal structure was evidenced for the $Ce_{0.15}Zr_{0.85}O_2$ sample. On the contrary, the structure of pure zirconia sample was monoclinic. As far acidic properties, the incorporation of increasing quantities of zirconium into the ceria lattice led to a marked increase in the total and strong acidity. Therefore, the highest and strongest acidity was found for $Ce_{0.15}Zr_{0.85}O_2$ mixed oxide. On the other hand, the redox process was found to be promoted in the mixed oxides with respect to the pure cerium oxide. Thus, insertion of ZrO_2 into the cubic CeO_2 resulted in a distortion on the mixed oxide, which allowed for a higher mobility of the lattice oxygen, and consequently reduction was no longer confined to the surface but extended deep into the bulk [6]. It was noted that the extent or the reduction and oxygen consumption was larger for the $Ce_{0.5}Zr_{0.5}O_2$ sample. Since the charge/radius of Ce^{3+} (radius 1.14 Å) is significantly lower than that of Ce^{4+} (radius 0.97 Å), the formation of vacancies or structural defects was promoted, and as a result the oxygen mobility was favoured [7]. It is important to remark that this promotion was not evident at temperatures lower than 300°C.

Activity results from the fixed-bed reactor evidenced that TOL was more reactive than HEX irrespective of the catalyst examined. The higher reactivity could be explained in terms of the lower C–H bond strength of the TOL compared with that of HEX [8]. As for catalyst composition, it was found that CeO_2 was the most active catalyst for the combustion of both hydrocarbons, since the major oxidation products (CO_2 and H_2O) were noticed at lower temperature (<250°C). However, the mixed oxides did not show any improvement in conversion with respect to the parent pure oxide. This observation suggested that surface oxygen species, which were more abundant on CeO_2, were sufficiently active for hydrocarbon conversion [9]. In this sense, Long *et al.* [10] reported that ceria would activate oxygen species on the surface such as O_2^{2-} at temperature lower than 150°C. Furthermore, acid sites on the mixed oxides acted as chemisorption sites thereby inhibiting the combustion reaction. This was in agreement with the negligible activity shown by the pure zirconia.

The adsorption and subsequent temperature-programmed decomposition followed by evolved gas analysis (mass spectrometry) was investigated over various catalysts as well. Table 2 reveals that HEX was adsorbed to a major extent in comparison with TOL, irrespectively of the catalyst, and that ceria exhibited the lowest adsorption capacity of both compounds, being virtually negligible in the case of TOL. Therefore, it was suggested that the higher catalyst acidity, in other words, the higher zirconia content, the larger interaction of hydrocarbons with the catalyst surface. This notable interaction stabilised the compound on the catalyst surface thereby decreasing their reactivity. As a result, higher temperatures were required for their de-

Table 1 Main physico-chemical properties of oxide catalysts

	BET surface area/ $m^2\ g^{-1}$	Pore volume/ $cm^3\ g^{-1}$	Average pore size/ Å	Lattice parameter/ Å	Structure	Acidity/mmol $NH_3\ g^{-1}$		H_2 consumption/ mmol g^{-1}	OSC/ mmol g^{-1}
						total	strong		
CeO_2	99	0.21	59	5.41	cubic	0.17	0.03	0.20	0.05
$Ce_{0.8}Zr_{0.2}O_2$	102	0.18	48	5.35	cubic	0.24	0.09	1.00	0.32
$Ce_{0.68}Zr_{0.32}O_2$	101	0.24	70	5.30	cubic	0.26	0.10	1.29	0.41
$Ce_{0.50}Zr_{0.50}O_2$	99	0.21	64	5.26	tetragonal	0.31	0.13	1.32	0.45
$Ce_{0.15}Zr_{0.85}O_2$	86	0.28	102	5.14	tetragonal	0.35	0.15	0.51	0.18
ZrO_2	51	0.25	157	–	monoclinic	0.24	0.11	–	–

composition [11]. Hence, acidity appeared not to be an adequate catalytic characteristic.

Figure 1 shows the results from the temperature-programmed oxidation of TOL and HEX over CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ samples followed by thermal conductivity and mass spectroscopy. For the CeO_2 sample, both HEX (mass 57) and TOL (mass 91) desorption were evident at low temperatures (~150°C). However, both compounds were decomposed at higher temperatures (>200°C) as revealed by the presence of carbon dioxide (mass 44) and water (mass 18). In contrast, the experiment carried out with the $Ce_{0.5}Zr_{0.5}O_2$ sample evidenced that the desorption of both compounds was noticeable over the whole temperature range, and appreciable conversions were only noticed at temperatures as high as 300–350°C. In the case of zirconia (not shown), the TCD signal was exclusively attributed to the hydrocarbons desorption. It was concluded that the decomposition of the adsorbed compounds over this catalyst required the existence of gas phase oxygen species. It is worth pointing out that these results were consistent with the catalytic activity trend found in the catalytic reaction runs.

Table 2 Adsorption capacity (mmol g^{-1}) of HEX and TOL over CeO_2, $Ce_{0.5}Zr_{0.5}O_2$ and ZrO_2 samples

Catalyst	CeO_2	$Ce_{0.5}Zr_{0.5}O_2$	ZrO_2
HEX	0.17	0.25	0.22
TOL	0.008	0.07	0.06

Moreover, a visual inspection of the samples once the experiments were concluded, gave evidence of a change in the colour of the oxides. Thus, the usual yellow colour characteristic of the oxidised samples turned into a greyish colour, which is related

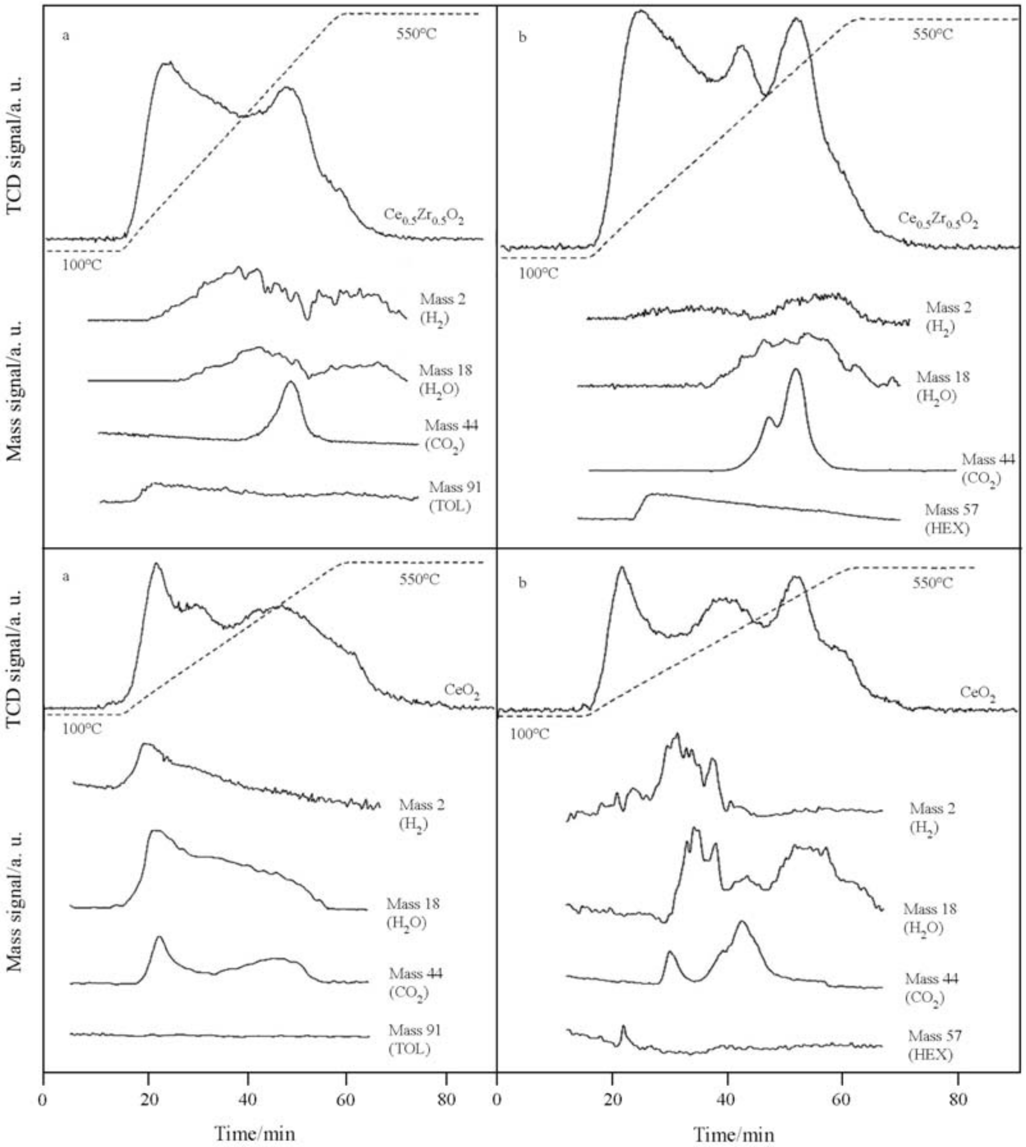

Fig. 1 Profiles of the temperature-programmed decomposition of adsorbed a – TOL and b – HEX over $Ce_{0.5}Zr_{0.5}O_2$ and b – CeO_2

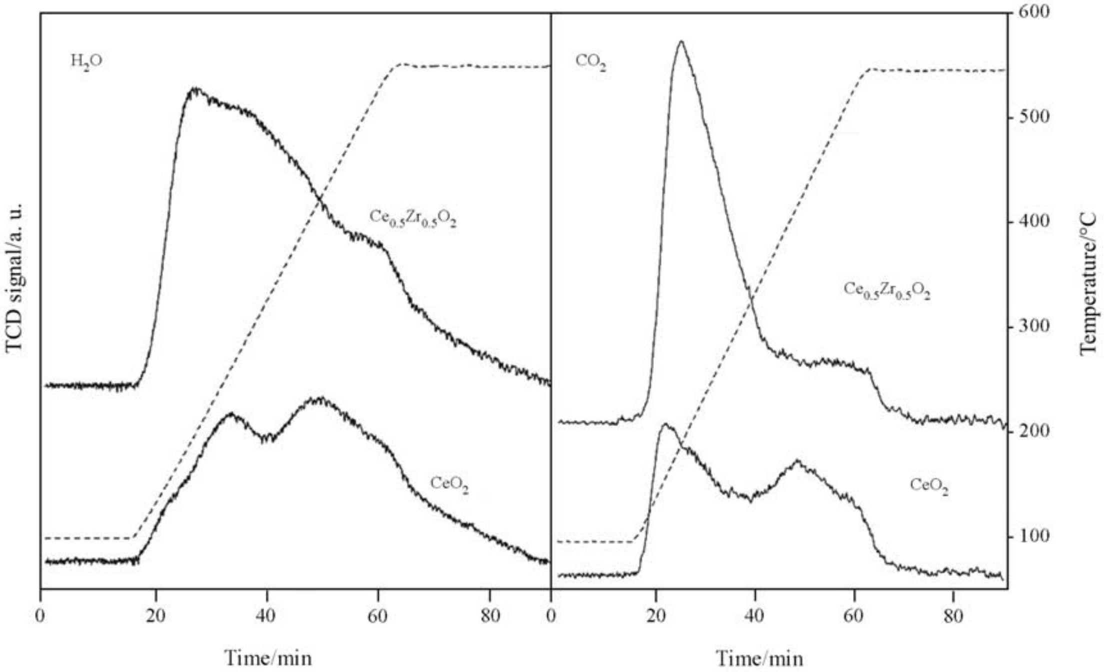

Fig. 2 H_2O-TPD and CO_2-TPD profiles of CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$

to reduced ceria-based materials [12]. In addition, H_2 (mass 2) was also detected in the effluent stream. This compound was generated as a result of the conversion of hydrogen atoms of HEX or TOL molecules in the absence of oxygen. Conversely, hydrogen was not detected in the product stream of the catalytic runs since the hydrogen atoms were easily converted to H_2O in an excess of oxygen (oxidative conditions).

Other factors may also play a significant role in the observed highly active catalytic behaviour of the CeO_2 sample with respect to the different mixed oxides. As aforementioned, HEX and TOL oxidations gave rise to notable amounts of CO_2 and H_2O as reaction products. These compounds could be eventually adsorbed on the catalyst surface leading to a negative impact on the catalytic activity. For instance, Auer *et al.* [13] associated the inhibition of the methane combustion in presence of ethylene with the generation of H_2O and CO_2 derived from the oxidation of the olefinic compound. In the same way, Zhang *et al.* [14] and Wu *et al.* [15] suggested that at low temperatures, the water vapour generated by VOC oxidation could be easily condensed in the pores due to the hydrophylicity of oxide supports.

The influence of the adsorption of both carbon dioxide and water on the catalytic performance of CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ samples was analysed by means of temperature-programmed desorption. The H_2O-TPD profiles (Fig. 2) evidenced a higher adsorption of water for the $Ce_{0.5}Zr_{0.5}O_2$ sample compared with that of the CeO_2 sample. Consequently, a higher activity inhibition would be expected when zirconia was incorporated into the ceria framework. Consequently, the hydrophobic nature of the catalyst should be beneficial in processes where high water concentrations are present by offering reduced sensitivity to water inhibition [16]. Similarly, the CO_2-TPD results (Fig. 2) showed that the mixed oxide preferentially adsorbed CO_2 with respect to the pure cerium oxide. In sum, the remarkable activity of CeO_2 for HEX and TOL conversion could also be explained on the basis of its reduced interaction with the main reaction products, CO_2 and H_2O, with the catalyst surface [17].

Conclusions

The catalytic behaviour of pure ceria, pure zirconia and a series of Ce/Zr mixed oxides in the oxidation of HEX and TOL was analysed by temperature-programmed oxidative degradation followed by TCD and mass spectrometry. It was concluded that acidity was not an appropriate catalyst property whereas surface oxygen species played a crucial catalytic role. CeO_2 resulted the most active catalyst for the combustion of the two VOCs, being TOL more reactive than HEX. On the other side, the presence of large amounts of water and carbon dioxide produced during reaction may be also responsible for the lower catalytic activity of mixed oxides.

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