



# On the activity of copper chromite catalysts in ethyl acetate combustion in the presence and absence of oxygen

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

## Abstract

The catalytic combustion of ethyl acetate has been investigated using undoped and Mn- or Ba-doped copper chromite catalysts either in the presence or in the absence of molecular oxygen.

The thermal reduction under hydrogen of undoped and Ba- or Mn-doped copper chromite system has been studied at different temperatures using the thermogravimetric technique. Evidences found by TG analyses (oxygen depletion rate) have shown a dependence on lattice oxygen mobility due to the crystal structure and the temperature. Relative to the undoped CuO-CuCr<sub>2</sub>O<sub>4</sub>, it has been found that the reduction rate is not significantly affected by the presence of BaO and MnO promoters but rather by the solid crystallinity.

The catalytic results have shown that good conversions can be obtained even at low temperatures (180–240 °C). While in the presence of molecular oxygen the only product observed was CO<sub>2</sub>, when the reaction has been carried out in the absence of oxygen (with lattice oxygen alone) noticeable amounts of CO were also detected. These results are consistent with the hypothesis of two different mechanisms controlling the reaction in the presence or in the absence of molecular oxygen. Further it has been observed that the catalytic activity becomes stable only when a specific Cu<sup>2+</sup>/Cu<sup>+</sup> ratio is obtained under typical reaction conditions.

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## 1. Introduction

Offensive odours and toxic air emissions as well as the formation of ground-level ozone and photochemical smog are environmental problems which are related to emissions of VOCs. To reduce the environ-

mental impact of their emissions and be able to fulfil established goals regarding the reduction of VOCs the legislation which already partly has been introduced will become more stringent. VOCs catalytic combustion is gaining increasing importance in the pollution control of industrial effluents [1]. Among VOC, ethyl acetate, a key component in ink manufacture, is oxidised to CO<sub>2</sub> using Pd, Pt supported on  $\gamma$ -alumina catalysts operating at a temperature range of 220–320 °C [2].

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According to McCabe and Mitchell [3] and Yu Yao [4] Pt/Al<sub>2</sub>O<sub>3</sub> catalysts are in general slightly more active than base metal oxides catalysts on the same GHSV.

However, base metal oxides catalysts may be an alternative due to the fact that these are much cheaper than Pt, allowing a higher catalysts load. A high loading of active phase also make the catalyst less sensitive than the platinum catalyst to non-selective poisoning, so that a great interest has turned to oxide-based catalysts. Simple metal oxides containing elements that can undergo red–ox cycles varying their valence state are the most interesting ones. Mixed oxides show better activity than the single oxides one [5,6]. Among these catalysts the copper-based oxides seem to be promising for the VOCs total combustion [7–9].

Although VOCs combustion has been widely investigated using metal oxide-based catalysts [1] as an alternative to noble metals, the development of a total oxidation catalyst is still a challenging subject to be solved.

Herewith, we report the oxidation of ethyl acetate using copper chromite-based catalysts (CuO–CuCr<sub>2</sub>O<sub>4</sub>), which are successfully used for the catalytic combustion of methanol, ethanol, and acetaldehyde [7]. Undoped and doped Mn or Ba copper chromite catalysts have been tested with both lattice oxygen (of the copper species) and molecular oxygen (of the feed mixture).

## 2. Experimental

### 2.1. Catalysts characterisation

Copper chromite-based catalysts have been purchased from Alpha products (CuO–CuCr<sub>2</sub>O<sub>4</sub>-I, Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-II, Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-III) and

Engelhard (Mn/CuO–CuCr<sub>2</sub>O<sub>4</sub>-IV). The chemical composition and specific surface area (BET) of the products are given in Table 1.

Thermal studies of the compounds have been carried out on a Seiko TG–DTA instrument. Weighed samples (ca. 20 mg) have been placed in alumina crucibles and reduction tests have been carried out under a hydrogen atmosphere (gas feed 61 h<sup>-1</sup>) while recording the TG–DTA and DTG curves.

Porosimetry and BET surface measurements have been performed on a Quantasorb (Quantachrome Co.) instrument.

X-ray diffraction (XRD) patterns of the samples have been recorded using a Siemens D 5000 diffractometer with filtered Cu K $\alpha$  radiation (count time of 1 s in the range 2 $\theta$  10–70°).

Scanning electron micrographs of samples have been recorded using a Zeiss DSM 940 apparatus.

XPS analyses have been carried out using a surface Science Instrument M-probe. The system was equipped with a reaction chamber where the sample could be heated and treated with gases.

The source for the XPS spectra is monochromatic Al K $\alpha$  radiation (1486.6 eV). A spot size of 200  $\mu$ m  $\times$  750  $\mu$ m and a pass energy of 25 eV are used with a resolution of 0.74 eV. An argon ion gun (VG EX05, 5 keV) to clean the metal foils and an electron flood gun (electron energy 3 eV) have been used to compensate the accumulation of positive charges.

The energy scale is calibrated with reference to the 2P<sub>3/2</sub> level (932.47  $\pm$  0.07 eV) and to the 3s level (122.39  $\pm$  0.15 eV) of a sputtered copper foil and to the 4f<sub>7/2</sub> level of a freshly evaporated gold film (84.00  $\pm$  0.10 eV). For internal reference the 1s level of carbon in hydrocarbon contaminants always present is taken as 284.6 eV. The reported binding energy values are  $\pm$ 0.2 eV, while the atomic percentages are estimated to be  $\pm$ 3%.

Table 1  
Composition, surface area and porosimetry data of copper chromite-based catalysts

Catalysts	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	Bulk composition (%)				Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Cumulative pores area (m <sup>2</sup> g <sup>-1</sup> )	Medium radius (Å)
		CuO (Cu*)	Cr <sub>2</sub> O <sub>3</sub> (Cr*)	BaO (Ba)	MnO (Mn*)			
CuO–CuCr <sub>2</sub> O <sub>4</sub> -I	35.2	51	49	–	–	0.123	29.2	84.7
Ba/CuO–CuCr <sub>2</sub> O <sub>4</sub> -II	54.5	39	43.5	10	–	0.186	60.4	61.6
Ba/CuO–CuCr <sub>2</sub> O <sub>4</sub> -III	4.8	39	43.5	10	–	0.006	2.05	61.2
Mn/CuO–CuCr <sub>2</sub> O <sub>4</sub> -IV	36.1	36*	33*	–	3*	0.187	34.1	109

## 2.2. Catalytic tests

### 2.2.1. In the presence of molecular oxygen

Catalytic runs have been carried out in a continuous flow-system consisting in a quartz fixed-bed tubular reactor (total volume = 30 cm<sup>3</sup>, length of the catalytic zone  $l = 10$  cm, diameter = 1 cm). The catalyst (ca. 1 g) was mixed with silicon carbide powder (ca. 10 g) of similar size. The catalyst was preheated to 150 °C under an ethyl acetate and helium stream for about 30 min in order to obtain a constant concentration of ethyl acetate (8.3–12 g N<sup>-1</sup> m<sup>-3</sup>) in the system. The reactor was then heated to the desired temperature and molecular oxygen (18%) was fed to the system.

Preliminary tests have been carried out to verify the absence of diffusional limitations. Several runs have thus been performed by varying both the flow rate and the catalyst weight while maintaining the same contact time. Tests have also been carried out using different particle sizes (180–325 mesh) of the same catalyst. These tests have shown that the ethyl acetate conversion and the product distribution remain constant.

### 2.2.2. In the absence of molecular oxygen

In this case in the absence of oxygen the continuous flow consisted of ethyl acetate 3% and helium 97%. The runs have been carried out maintaining the same contact times adopted in the presence of molecular oxygen. The reaction products have been sampled using a Valco 16 positions valve.

In both cases (in the presence or in the absence of molecular oxygen) the reaction products (CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, (CH<sub>3</sub>)<sub>2</sub>CO and C<sub>2</sub>H<sub>4</sub>O) have been analysed on-line by gas chromatography. While oxygen and carbon monoxide have been analysed using a molecular sieve 5 Å column connected to a thermal conductivity detector (TCD), ethanol, acetone and acetaldehyde have been analysed by a Porapak QS column linked both to a flame ionisation (FID) and to a thermal conductivity (TCD) detectors.

## 3. Results and discussion

### 3.1. Thermoanalytic study of the Cu-Cr-O-based systems

The thermal reduction of copper chromite Cu-Cr-O-based systems has been performed under hydrogen at

a temperature ranging from 25 to 600 °C. The effect of the increasing temperature on the reduction behaviour of the undoped and Ba- or Mn-doped CuO-CuCr<sub>2</sub>O<sub>4</sub> phases has been studied.

The trend of the TG curves which indicating the increase of oxygen mobility with temperature evidences the presence of two types of lattice oxygen in the solids; the oxygen present in CuO and in CuCr<sub>2</sub>O<sub>4</sub>.

A comparison of the reduction trends of CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II, Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III, and Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV catalysts at temperature ranging from 25 to 500 °C has shown that while the depletion rate between 150 and 220 °C is similar for all the catalysts, between 220 and 500 °C it evolves in the following order: CuO-CuCr<sub>2</sub>O<sub>4</sub>-I > Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV > Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II > Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III. These behaviours may be attributed to the different strength of Cu-O bonds in CuCr<sub>2</sub>O<sub>4</sub> in the corresponding catalysts which can be affected by doping elements.

The data relative to the three catalysts of major interest are given in Fig. 1 (maximum of the DTG peaks are ordered as follow CuO-CuCr<sub>2</sub>O<sub>4</sub>-I (176 °C) > Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II (172 °C) > Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV (174 and 164 °C). The reduction temperature of pure CuO (198 °C) and Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III (205 °C) serve as references and comparisons. It is worth nothing that:

- the reduction temperature of the three catalysts CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II and Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV is lower than the temperature of pure oxide;
- catalyst Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV shows two DTG peaks corresponding to two DTA peaks.

### 3.2. XRD characterisation of the catalysts

XRD spectra (Fig. 2) of CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV, Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II, and Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III have been found to be different from one another especially those containing barium oxide. With respect to the CuO-CuCr<sub>2</sub>O<sub>4</sub>-I catalyst Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II presents several peaks at  $2\theta$  ranging from 20 to 45 with a wide peak around  $2\theta$  of 35 characteristic of CuO. Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III is well crystallised and presents peaks characteristic of CuO ( $2\theta$  equal to 35.48 and 38.82°), CuCr<sub>2</sub>O<sub>4</sub>

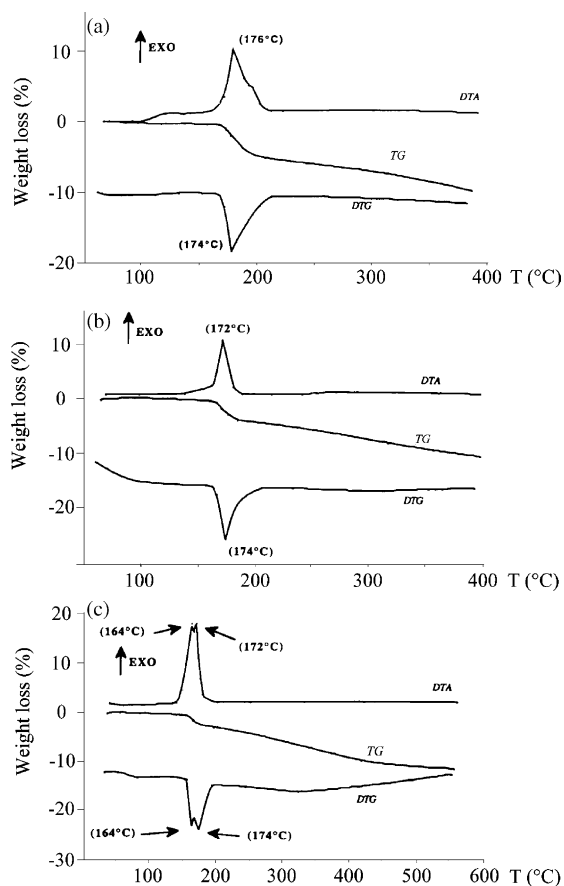


Fig. 1. TG–DTA–DTG of (a) CuO–CuCr<sub>2</sub>O<sub>4</sub>-I, (b) Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-II and (c) Mn/CuO–CuCr<sub>2</sub>O<sub>4</sub>-IV under hydrogen.

(35.28 and 37.71°) and BaCrO<sub>4</sub> (25.35, 28.17, 30, 91 and 42.10°).

### 3.2.1. Porosimetry measurements

The pore volume distribution, the form of hysteresis loop and the pore size distribution versus mean pore radius has been recorded for all the catalytic systems (CuO–CuCr<sub>2</sub>O<sub>4</sub>-I, Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-II, Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-III, and Mn/CuO–CuCr<sub>2</sub>O<sub>4</sub>-IV). The doped copper chromite catalyst (Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-II, Mn/CuO–CuCr<sub>2</sub>O<sub>4</sub>-IV) showed a predominantly microporous pore volume distribution with a total pore volume and a total pore surface area, respectively, higher than the corresponding undoped product (Table 1).

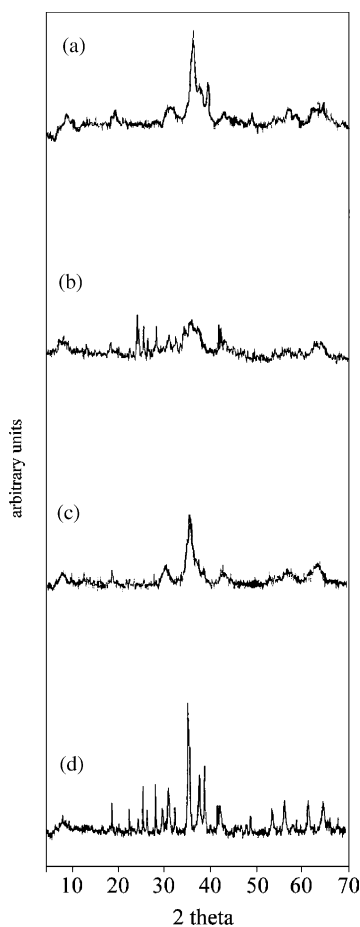


Fig. 2. XRD of (a) CuO–CuCr<sub>2</sub>O<sub>4</sub>-I, (b) Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-II, (c) Mn/CuO–CuCr<sub>2</sub>O<sub>4</sub>-IV and (d) Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-III.

The evolution of adsorption and desorption isotherms of nitrogen has been recorded at 77 K for CuO–CuCr<sub>2</sub>O<sub>4</sub>-I, Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-II, Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-III, and Mn/CuO–CuCr<sub>2</sub>O<sub>4</sub>-IV catalysts [10]. The hysteresis loop obtained for the doped catalysts is spread over a  $P/P_0$  range from about 0.4 to 0.98 with a vertical form for CuO–CuCr<sub>2</sub>O<sub>4</sub>-I and Mn/CuO–CuCr<sub>2</sub>O<sub>4</sub>-IV and a less pronounced vertical form for both Ba-doped catalysts in the same  $P/P_0$  interval.

It has also been noticed that the loop formed by the adsorption and desorption curves is more or less important according to the nature of the catalyst except the well crystallised Ba/CuO–CuCr<sub>2</sub>O<sub>4</sub>-III where the adsorption and desorption curves are superposed.

Table 2

XPS data of CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV and Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II systems

Catalysts	Surface composition						Cu <sup>2+</sup> /Cu <sup>+</sup>		Cr <sup>6+</sup> /Cr <sup>3+</sup>	
	%Cu	%Cr	%Mn	%Ba	%O	%C	Fresh catalyst	Used catalyst	Fresh catalyst	Used catalyst
CuO-CuCr <sub>2</sub> O <sub>4</sub> -I	9.3	13.9	–	–	61.4	15.4	0.8752	0.3511	0.3917	0.2360
Ba/CuO-CuCr <sub>2</sub> O <sub>4</sub> -II	13.2	13.1	–	0.7	55.9	17.0	1.8328	0.9972	0.2517	0.2873
Mn/CuO-CuCr <sub>2</sub> O <sub>4</sub> -IV	7.2	16.2	3.2	–	57.0	16.4	0.5218	0.2052	0.2594	0.2800

This difference may be due both to the presence of a small total pore surface area and pore volume in the Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III catalyst and to a different pore structure [11,12]. Table 1 report some porosimetry data characteristic of the studied catalysts.

### 3.3. Surface analysis

CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II and Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV samples have been analysed by X-ray photoelectron spectroscopy (XPS). The surface composition of the catalysts together with the relative oxidation states of the species present are reported in Table 2. As it can be noticed the amount of copper in the surface composition is more decisive in the case of Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II than Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV and CuO-CuCr<sub>2</sub>O<sub>4</sub>-I catalysts. The low value of Ba with Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II system can be noticed too. This indicates that the Ba species are incorporated inside CuO-CuCr<sub>2</sub>O<sub>4</sub> in large part.

Cu<sup>2+</sup> and Cu<sup>+</sup> species on the surface of fresh and used catalysts have also been noticed (Table 2). When

ever metallic copper is present in low concentration, due to the reaction medium which is rich in oxygen, Cu peaks, which might also be present, cannot be discerned since the Cu 2p of metals and the Cu<sup>+</sup> of the oxides are difficult to distinguish using XPS instead of Auger technique.

When comparing the Cu<sup>2+</sup>/Cu<sup>+</sup> and the Cr<sup>6+</sup>/Cr<sup>3+</sup> ratios of both fresh and used catalysts, these latter show a marked increase in the amount of Cu<sup>+</sup> during the reaction (Table 2). This change in the Cu concentration species might be correlated with the reactivity of the studied systems (Fig. 3 and Table 3).

### 3.4. Catalytic tests

Space velocities varying in the interval 2500–10,000 h<sup>-1</sup>, which are at the lowest limit in the field of industrial applicability have been employed. We have investigated the effects of the concentration of ethyl acetate on conversion and selectivity, feeding concentrations of 4.9 and 19.9 g N<sup>-1</sup> m<sup>-3</sup> and have observed that the increase in concentration

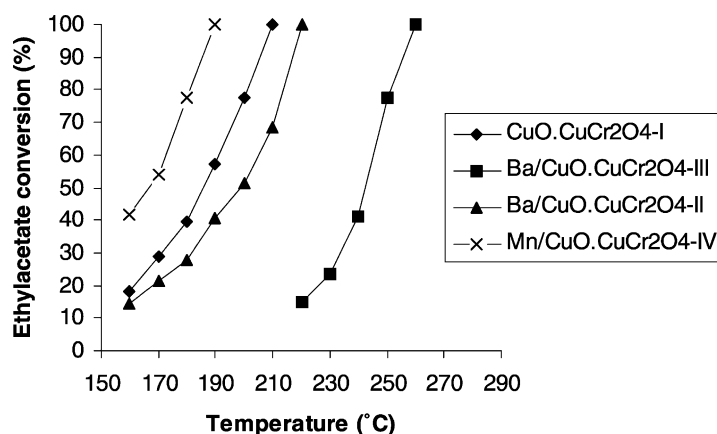


Fig. 3. Catalytic activity of undoped and doped copper chromite catalysts ( $F = 51 \text{ h}^{-1}$ , catalyst weight = 1 g mixed with silicon carbide).

Table 3

Catalytic activity of copper chromite-based systems in presence of molecular oxygen

Catalyst	% Conversion	Temperature (°C)	Intrinsic activity (mol h <sup>-1</sup> m <sup>-2</sup> )
Mn/CuO-CuCr <sub>2</sub> O <sub>4</sub> -IV	77.3	180	5.95 × 10 <sup>-3</sup>
CuO-CuCr <sub>2</sub> O <sub>4</sub> -I	39.4	180	3.11 × 10 <sup>-3</sup>
Ba/CuO-CuCr <sub>2</sub> O <sub>4</sub> -II	28.1	180	1.98 × 10 <sup>-3</sup>
Ba/CuO-CuCr <sub>2</sub> O <sub>4</sub> -III	15.1	220	1.03 × 10 <sup>-3</sup>

$F = 5 \text{ h}^{-1}$ , 1 g of catalyst mixed with silicon carbide of the same size.

requires an increase of 10–20 °C in the temperature needed for a total combustion (210 °C versus 220 °C for ethylacetate concentrations, respectively, of 4.9 and 19.9 g N<sup>-1</sup> m<sup>-3</sup> using CuO-CuCr<sub>2</sub>O<sub>4</sub>-I catalyst, 190 °C versus 200 °C with Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV, and 200 °C versus 210 °C with of Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II catalyst), while it does not make any impact on selectivity (100% CO<sub>2</sub> selectivity). According to the data reported in Fig. 3, it can be noticed that the conversion of ethyl acetate for the production of CO<sub>2</sub> are increased at the same time as temperature. The reaction of total combustion are facilitated to a greater extent than partial oxidations (acetaldehyde as a reaction intermediate is always present when ethyl acetate conversion is not total). An increase in contact time  $W/F$  (catalyst weight/flow rate of carrier gas) from 0.5 to  $2 \times 10^{-1} \text{ g l}^{-1} \text{ h}$  allows a higher conversion to take place at the same temperature and therefore a total combustion at a lower temperature (at 180 °C, 39.4% versus 27.1% with CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, 77.3% versus 51.4% at 180 °C using Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV and 28.1% versus 15.3% Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II using  $W/F$  of 2 and  $0.5 \times 10^{-1} \text{ g l}^{-1} \text{ h}$ , respectively. We have reached similar results with contact time of  $10^{-1}$  and  $0.5 \times 10^{-1} \text{ g l}^{-1} \text{ h}$ . The values of the concentrations of ethyl acetate far exceed those that can be verified industrially and have been chosen to emphasise the possible effects on combustion depending on the variable quantities of pollutants.

On the basis of the obtained results the Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV catalyst has turned out to be more active than CuO-CuCr<sub>2</sub>O<sub>4</sub>-I catalyst with equal surface area. The Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III has proved less active than the catalyst without a promoter (Table 3). In fact, the reduction data with H<sub>2</sub> (Fig. 1) make it possible to correlate the data of the catalytic activity to the liability of lattice oxygen. It is reasonable to assume that in the case of catalyst IV the MnO<sub>x</sub> species are responsible

for a major liability of lattice oxygen (DTG peaks at 164 and 174 °C). This fact might be ascribed to the combined effect of MnO<sub>x</sub> and CuO in catalyst Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV.

According to the XPS analyses, manganese is present on the surface in much bigger quantities, even if it is present in the matrix in lower amounts than barium (3% versus 10%). Besides it appears that manganese is present in the form of oxide, while barium has been identified as barium chromate.

The catalysts have given fairly different results as regards the evolution of conversion and selectivity when temperature changes. The production of acetaldehyde has resulted considerable (58% for Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV, 62% for CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, 72% Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II and 81% for Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III at a temperature of 180 °C) except when the combustion of ethyl acetate is total. The products of partial oxidation, such as acetaldehyde, are thermodynamically unstable if compared to those of total combustion; their concentration in the mixture of the reaction products is also relative to contact time [7,9]. The presence of other intermediates is negligible: ethanol (Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II catalysts) and acetone are present in very small quantities, while other possible products (acetic acid, diethyl ether) have not been formed in agreement with the data regarding the reactivity order on CuO-based catalysts of the C<sub>2</sub> species present in literature [9]. It is notable that in the final phase of the reaction there is an abrupt increase in the conversion which concentrates at 10 °C.

Combustion tests especially carried out on ethanol and acetone in similar concentrations as those employed for ethyl acetate, have shown that the total combustion of these two pure products takes place at lower temperatures (160 and 180 °C, respectively).

In order to investigate a possible red-ox mechanism for the reaction we have carried out Mn/CuO-

Table 4  
Catalytic results obtained with Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV in absence of oxygen

Time (min)	% Conversion	% Selectivity				
		CO <sub>2</sub>	CO	CH <sub>3</sub> CHO	C <sub>2</sub> H <sub>5</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CO
0	100	77	23	–	–	–
30	100	53	47	–	–	–
60	42.3	11	4	72	–	13
90	14.8	–	–	78	5	17

$F = 51 \text{ h}^{-1}$ , 1 g of catalyst,  $T = 180^\circ\text{C}$ .

CuCr<sub>2</sub>O<sub>4</sub>-IV catalytic tests in the absence of oxygen and have found a difference in them, that is, CO is present as well as CO<sub>2</sub>. It may mean that the oxygen of the reaction mixture makes the CO → CO<sub>2</sub> reaction faster, besides participating in the red–ox cycle (Table 4).

With regard to this it should be noticed that Severino et al. claim that the CO → CO<sub>2</sub> oxidation takes place more effectively on CuCr<sub>2</sub>O<sub>4</sub> catalysts than CuO catalysts [13,14]. As time passes and lattice oxygen decreases, the presence of organic intermediates of combustion gets more evident in comparison with the tests carried out in the presence of oxygen. Moreover, after re-oxidation at the same temperature as the reaction, the catalyst starts functioning as before.

The results reported in this work agree with those present in literature concerning the oxidation of formic acid, methyl alcohol, ethanol, acetic acid and acetaldehyde on alumina-supported CuO where combustion has been ascribed to the lattice oxygen of CuO [8].

The tests carried out on Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV catalyst previously treated with HCl, HNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> alternatively, so as to eliminate CuO from chromite, have shown a drastic fall in the activity (from 100 to ca. 2% at 190 °C) suggesting that the active phase is constituted by CuO-phase.

In order to explain the different catalytic behaviour of the CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II, Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III and Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV samples, the following point should be taken into account:

- (a) from the observation of the different diffraction patterns it is clear that while in the Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III catalysts CuO is present as a well crystallised form, in the other three it is present as non-well-crystallised phase;

- (b) according to the XPS results it can be inferred that the Cu<sup>2+</sup>/Cu<sup>+</sup> ratio shows a decreasing scale on the samples from Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III to CuO-CuCr<sub>2</sub>O<sub>4</sub>-I to Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV either before or after the reactivity tests.

Actually the three samples Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV, CuO-CuCr<sub>2</sub>O<sub>4</sub>-I and Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III show an intrinsic activity decreasing from Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV to Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II, which is however definitely more active than Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III. This fact might be explained by the presence of a CuO-crystallised phase in the Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-III sample (point a); as for different reactivity of the CuO-CuCr<sub>2</sub>O<sub>4</sub>-I, Mn/CuO-CuCr<sub>2</sub>O<sub>4</sub>-IV and Ba/CuO-CuCr<sub>2</sub>O<sub>4</sub>-II catalysts, in which CuO is present with a non-well-crystallised phase, the order of intrinsic activity could be explained by means of a Cu<sup>2+</sup>/Cu<sup>+</sup> scale verified by XPS.

It is well known that the activity of pure and mixed oxide-based catalysts depends on the presence of red–ox couples [5,6] and it has been suggested that the higher catalytic activity and the lower value of the Cu<sup>2+</sup>/Cu<sup>+</sup> ratio of two compared copper chromite-based catalysts are correlated [15].

On the basis of these considerations it seems possible to propose a reactivity scale related to a different Cu<sup>2+</sup>/Cu<sup>+</sup> surface ratio.

From the observation of the results obtained it comes out that:

- in the presence of oxygen and with the total conversion of ethyl acetate the total combustion takes place;
- in the absence of oxygen only the total conversion of ethyl acetate occurs;
- catalysts are no longer active for combustion after acid and alkaline washings carried out to eliminate CuO.

Taking these points into account and also considering that some authors [13,14] have used acid or alkaline washings to prove that CuCr<sub>2</sub>O<sub>4</sub> is the most active catalysts for the CO → CO<sub>2</sub> oxidation, it can be claimed that the lattice oxygen of CuO allows the oxidation of ethyl acetate to take place, but it does not permit the total transformation from CO to CO<sub>2</sub>. Therefore, the presence of Cu in a CuCr<sub>2</sub>O<sub>4</sub> catalyst is absolutely necessary.

#### 4. Conclusions

from the above reported results it can be concluded that:

- the studied copper chromite-based catalysts are interesting for the total combustion of ethyl acetate;
- a red–ox mechanism is consistent with the ethylacetate combustion and it mainly concerns the CuO-phase. This has also been confirmed by totally removing CuO before use with acid or alkaline solutions;
- if the ethylacetate combustion is carried out in the presence of oxygen the total combustion of CO occurs without acetaldehyde formation and is probably due to  $\text{CuCr}_2\text{O}_4$  in agreement with previous findings;
- the incidence of the  $\text{Cu}^{2+}/\text{Cu}^+$  ratio on the intrinsic activity is a promising datum to realise the catalyst preparation and activation;
- the total combustion occurs in a range of temperatures which is compatible with the industrial requirements.

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