

Catalytic Abatement of VOCs: Aerobic Combustion of Methane or Ethane over Alumina-Supported Metal Oxides Recovered from Spent Catalysts

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Received: March 13, 2020

Accepted: April 8, 2020

Online Published: May 5, 2020

doi:10.5539/enrr.v10n2p33

URL: <https://doi.org/10.5539/enrr.v10n2p33>

Abstract

γ -Al₂O₃ supported Cu, Cu-Zn and Cu-Ni-Fe-Zn oxide catalysts were prepared using leachate transition metal nitrate and sulfate aqueous solutions from commercial spent catalysts. A bench-scale rig was used to investigate the combustion activity of these catalysts toward methane or ethane in the air stream (1000 ppmv) at a space velocity of 20,000 h⁻¹. The Cu-Ni-Fe-Zn oxides/ γ -Al₂O₃ catalyst proved to be the most active catalyst for the combustion of methane in the temperature range 290-575°C and of ethane in the lower temperature range of 275-525°C as compared to Cu and Cu-Zn oxide loaded catalysts. X-ray powder diffractograms indicated that the metal oxide species were highly dispersed or amorphous on the alumina surface in all the catalysts except for the detection of a minority phase of monoclinic CuO on the Cu-containing mono-metallic catalysts. The co-existence of ZnO in the CuO catalysts suppresses the activity of the copper oxide species and, therefore, the conversion of methane or ethane was reduced. The present research endeavor provides proof-of-concept that relatively inexpensive metal oxide-based heterogeneous catalysts for VOCs abatement can be recovered from spent catalysts. Hence, environmental and health threats of improper handling of VOCs or spent catalysts may be alleviated.

Keywords: Recycled Metal Oxide Catalysts, Spent Catalysts, Catalytic Combustion of Methane and Ethane, X-Ray Powder Diffractometry, Supported Cu Oxide Catalysts, Supported Cu-Ni-Fe-Zn Oxide Catalyst

1. Introduction

Volatile organic compounds (VOCs) are recognized as a major threat both to the environment and human health (Spivey, 1987; Liotta, 2010). VOCs include hydrocarbons (HCs) and hetero-atom containing organic compounds. Catalytic combustion (i.e., total oxidation) has become a favorable alternative to thermal oxidation as an effective method for the elimination of the usually low-concentrated VOCs in air streams. The key advantages of using catalytic combustion, compared with other decontamination technologies, include: (i) high efficiency at low pollutant concentrations, (ii) low energy consumption, and (iii) low formation rates of secondary pollutants, e.g. noxious nitrogen oxide (Morales *et al.*, 2008).

Unlike condensation and adsorption technologies, catalytic combustion does not reform HC pollutants but oxidizes them completely into CO₂ and H₂O, which are environmentally much less harmful materials. Supported noble metals (Diehl *et al.*, 2010; [5] Kim & Ahn, 2009; Shim *et al.*, 2008), metal oxides (Todorova *et al.*, 2010; Kim, 2002; Spivey & Butt, 1992; Kim & Shim, 2010) and mixed metal oxides (Kim & Ihm, 2001; Mu *et al.*, 2008; Jiráková *et al.*, 2009) have been widely employed for the catalytic combustion of VOCs. Even though transition metal oxides are less active catalysts than noble metals, they are cost-effective, environmentally friendly, and more resistant to poisoning and sintering than the noble metals (Morales *et al.*, 2008; Spivey & Butt, 1992; Vu *et al.*, 2008). Recently, Kamal *et al.* (2016) and Zhang *et al.* (2016) reviewed the elimination of VOCs using different catalytic oxidation processes with noble metal and metal oxide catalysts.

It is important to reduce methane and ethane emissions into the atmosphere; therefore, the present investigation was designed to focus on the combustion of methane and ethane in air. Although methane is the least reactive of the hydrocarbons, and therefore the most difficult to oxidize, the legislation on its emission still requires the

removal of trace amounts of it. SnO₂ has shown some activity by itself in the combustion of methane (Cullis & Willatt, 1983). Xiao *et al.* (2001) reported that cobalt oxides supported on ZrO₂ have higher oxidation activity than not only cobalt oxides supported on TiO₂, Al₂O₃ or MgO catalysts, but also than the bulk Co₃O₄. Li *et al.* (2009) observed that a mixed Co-Mn oxide catalyst with a Co/Mn molar ratio of 5, prepared by the co-precipitation method, facilitated 90% oxidation of methane at 320°C. Also, Chen *et al.* (2013) prepared Co-Cr mixed oxide catalyst with a Co/Cr molar ratio of 0.5, by co-precipitation, and found it to accomplish 90% oxidation at 464°C.

With respect to the catalytic combustion of ethane, several studies have been performed on using supported Pt and Pd catalysts (Noordally *et al.*, 1993; Tahir & Koh, 1996). Kucherov *et al.* (1996) observed that a Cu-ZSM-5 catalyst facilitated the oxidation of ethane in the air at 500-650°C. MnO₂ (4 wt.-%-Mn)/SnO₂ catalyst prepared by impregnation showed very high activity in the total oxidation of 0.2 vol.% ethane in the air (Tahir & Koh, 1997). Other investigations on ethane have been carried out using different transition metal oxides mounted on SnO₂. Supported metal oxide catalysts, such as Mn, Co, Cu, Ce, and Ni were studied and showed that Mn and Co oxides were the most active catalysts in the combustion of ethane at 420-440°C (Tahir & Koh, 1997). The total oxidation of ethane over Pd/ α -Al₂O₃ in an oxygen-rich atmosphere showed more activity after reduction with hydrogen at 300°C, and the rate of reaction was found to depend on the total amount of Pd (Anderson *et al.*, 1961).

There is a constant need in the field of VOCs abatement for developing cost-effective catalysts of high activity and durability. Therefore, using transition metal ions recovered from spent commercial catalysts, which were used in chemically-related applications, to produce metal oxide-based active catalysts for VOCs combustion is worth attempting for the following environmental advantages: (i) VOCs abatement in air, and (ii) avoiding improper disposal of the spent catalysts.

Therefore, the present investigation was designed to undertake the following studies. Recovery of transition metal ions (Cu, Ni, Fe, and Zn) from commercial spent catalysts via acid (HNO₃ or H₂SO₄) based traditional extraction method. Preparation of γ -Al₂O₃-supported oxides via (i) impregnation of the support with the nitrate or sulfate solutions of the recovered metal ions, and (ii) subsequent calcination at 450 or 650°C. Analogous sets of the catalysts were similarly prepared, but using impregnating solutions of commercial metal nitrates or sulfates, and handled as reference catalysts for control purposes. The prepared catalysts were characterized using atomic absorption spectroscopy for the determination of their transition metal contents, X-ray powder diffractometry for the elucidation of their crystalline phase composition, and (iii) N₂ sorptiometry for the determination of their BET-surface areas. Subsequently, the CH₄ and C₂H₆ combustion activity of the catalysts, whether the recycled or the reference catalysts, was measured employing a fixed-bed continuous flow reactor and gas chromatography.

2. Experimental

2.1 Catalysts Preparation

The used γ -Al₂O₃ support was obtained from UOP (UK). It was grounded to small particles of less than 0.5 mm in size before use, and found to assume a specific surface area of 120 m² g⁻¹. The impregnating solutions of Cu, Cu-Zn and Cu-Ni-Fe-Zn metal ions were obtained by leaching spent catalysts with nitric or sulfuric acids, adopting a traditional acid extraction technique (Askari, 2007; Li *et al.*, 2007; Arslan & Arslan, 2002). Typically, a 2-g portion of pulverized spent catalyst (supplied by Amlon Metal Limited (UK)) was mixed with 100 cm³ of the leach acid solution (69% HNO₃ or 98% H₂SO₄ (w/w) at fixed concentration of 3 mole dm⁻³) in a 0.5 dm³ flange flask. Then, the flask was placed on a hot plate for 1-2 hours at 50-75°C. The mixture was stirred using a magnetic stirrer. The leachate obtained was filtered and transferred to a 200 cm³ volumetric flask and made up to the mark with deionised water (final pH \leq 4). On the other hand, Cu, Ni, Fe and Zn nitrate and sulfate precursor compounds used to prepare reference catalysts (for control purposes) were 99.8%-pure Aldrich products. Their impregnating solutions were prepared in deionised water.

Supported Cu, Cu-Zn and Cu-Ni-Fe-Zn oxides catalysts were prepared by impregnating the γ -Al₂O₃ support particles with the metal ions aqueous solution (10 mL/g-Al₂O₃), whether the leachate or the commercial solution was used. The resultant suspension was stirred well, and the excess water removed/evaporated using a rotary evaporator. The solid product was dried further in air at 120°C for 24 h and, then, calcined in air at 450°C (for the nitrate solution) or 650°C (for the sulfate solution) for 5 h. When heated in air, CuSO₄ undergoes phase transitions, and, according to the literature (Arslan & Arslan, 2002; Abdel Basir & Rabah, 1999), converts into CuO at 650°C. For simplicity, each of the resulting catalysts is discerned below by a code number and a designation made-up of the chemical symbol(s) and amount(s) of the transition metal ions loaded, and the nature of the impregnating solution used. All recycled and reference catalysts prepared and examined in the present investigation are identified in Table 1.

Table 1. Catalyst code, elemental composition, impregnating solution used, and type

Code ^a	Composition ^b	Impregnating solution ^c	Type
Cat-1	Cu2.2Zn4.6	LNS	Recycled
Cat-2	Cu2.2Zn4.8	LSS	Recycled
Cat-3	Cu2.2Zn0.03	LSS	Recycled
Cat-4	Cu2.2	RNS	Reference
Cat-5	Cu5.0	RNS	Reference
Cat-6	Zn4.6	RNS	Reference
Cat-7	Cu0.11Ni1.9Fe0.3Zn0.14	LNS	Recycled
Cat-8	Cu2.2Zn4.6	RNS	Reference
Cat-9	Cu2.2Zn4.8	RSS	Reference
Cat-10	Cu0.11Ni1.9Fe0.3Zn0.14	RNS	Reference
Cat-0	γ -Al ₂ O ₃	-	Support

^aCatalysts 4-6 are mono-metallic; catalysts 1-3, 8 and 9 are bi-metallic; whereas catalysts 7 and 10 are quatio-metallic.

^bArabic numerals indicate amount (wt%) of the preceding metal ion

^cLNS = impregnated with leached metal nitrate solution;

LSS = impregnated with leached metal sulfate solution;

RNS = impregnated with commercial metal nitrate solution;

RSS = impregnated with commercial metal sulfate solution.

2.2 Catalysts Chacterization

Atomic absorption spectroscopy was carried out with a model Perkin-Elmer 2380 spectrometer. The Brunner-Emmett-Teller specific (BET) surface areas of all catalyst samples were determined via N₂ sorptiometry at liquid nitrogen temperature (- 196°C) using a Micromeritics ASAP 2020 analyzer. Prior to Nitrogen sorption analysis, all the samples were degassed under vacuum (5 x 10⁻³ mmHg) for 6 h at 250°C. X-ray powder diffractometry (XRD) was conducted employing a Philips PW1710 diffractomer equipped with Ni-filtered CuK_α radiation (λ = 0.15403 nm) operated at 40 keV and 30 mA. Test catalysts were investigated in the 2θ range of 4-100° at a scanning rate of 1.1°/h. Diffraction patterns thus obtained were matched with standard diffraction data (International Center for Diffraction data, 2018) for crystalline phase composition identification.

2.3 Catalytic Activity

Methane and ethane catalytic combustion experiments were carried out in a fixed-bed continuous flow quartz reactor (i.d. = 1.5 cm) operating under atmospheric pressure. The quartz reactor in the activity rig contained an inner quartz cup to hold the catalyst, which was housed in a tubular furnace. In each experiment, a 2-mL portion of catalyst was placed in the reactor supported by quartz wool. Thermocouples monitored the inlet and outlet temperatures, measuring the gas temperature. An on-line Perkin-Elmer F-11 gas chromatograph with a flame ionisation detector (FID) was used to monitor the total unburned hydrocarbon in the exit gas. In all activity tests performed, 1000 ppmv methane (or ethane) in air was fed into the reactor at a gas hourly space velocity of 20,000 h⁻¹ and the temperature range during the test was from 100 to 600°C, with 5 °C/min as ramping rate. The combustion products were CO₂ and H₂O, and other by-products were detectable under the experimental conditions applied. A blank test was conducted without a catalyst to examine the effect of the quartz wool and the quartz reactor and to confirm that no homogeneous reaction occurred below 600°C. The catalytic results obtained for methane (or ethane) as a function of the reaction temperature, collected after ensuring the steady state condition at a given temperature, resulted in S-shaped curves. The methane (or ethane) conversion% was calculated based on the hydrocarbon consumption:

$$Conversion(\%) = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

Where, C_i = inlet concentration of the VOC in the feed

C_o = outlet concentration of the VOC in the effluent.

3. Results and Discussion

3.1 Catalysts Elemental and Phase Compositions

Table 1, reveals that the test catalysts may be sub-grouped as mono-metallic (Cat-4 to Cat-6), bi-metallic (Cat-1 to Cat-3, and Cat-8 and Cat-9), and quater-metallic (Cat-7 and Cat-10) catalysts. Table 1 also reveals that the mono-metallic catalysts are reference catalysts, in which Cat-4 and Cat-5 contain different amounts of Cu ions, and Cat-6 contains Zn ions. However, the bi-metallic catalysts are identified to be either recycled (Cat-1 to Cat-3) or reference (Cat-8 and Cat-9) catalysts. In all the bi-metallic catalysts, the metallic constitution is made up of 2.2% Cu and 4.6-4.8% Zn ions, except for Cat-3 which has the same amount of Cu but only a scarce amount of Zn (0.03%) and the quater-metallic Cat-7 and Cat-10 are respectively recycled and reference catalysts each containing 0.11% Cu, 1.9% Ni, 0.3% Fe and 0.14% Zn. Table 1 reveals, moreover, that the metallic constitution of Cat-3 to Cat-5 is Cu-majored, and that of Cat-1, Cat-2, Cat-6, Cat-8 and Cat-9 is Zn-majored, whereas that of Cat-7 and Cat-10 is Ni-majored. It is worth noting, that the pure support (γ -Al₂O₃) is coded Cat-0 (Table 1).

The corresponding XRD results (Figure 1 and Table 2) indicate that except for Cat-1 and Cat-2, the bulk crystalline phase composition is either dominated (Cat-3) or majored (Cat-6 to Cat-10) by the γ -Al₂O₃ support. The minor crystalline phases identified are α -Al₂O₃ in Cat-3 and Cat-6 to Cat-10, and α -Al₂O₃ and m-CuO in both Cat-4 and Cat-5. Thus, the XRD results may suggest that the γ -Al₂O₃ support can strongly disperse up to the highest loading levels used of Zn, Ni and Fe, but cannot do likewise for $\geq 2.2\%$ Cu in its mono-metallic catalysts (Cat-4 and Cat-5). In the meantime, the γ -Al₂O₃ support is shown (Figure 1 and Table 2) to suffer a minor polymorphic transition (in Cat-3 to Cat-10) to the thermodynamically favorable α -Al₂O₃ phase (Wefers & Misra, 1987). The temperature regime ($\leq 650^\circ\text{C}$) at which this polymorphic transition commenced to occur is much less than that ($\geq 950^\circ\text{C}$) reported for the transition involving pure γ -Al₂O₃ (Wefers & Misra, 1987). This may help presuming that the minor γ -to- α -Al₂O₃ phase transition observed is, somehow, metal ion-assisted.

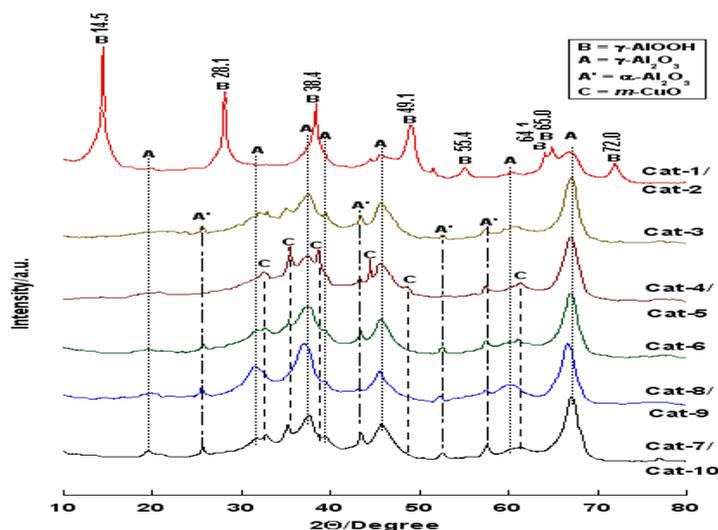


Figure 1. X-ray powder diffractograms obtained for the recycled and reference catalysts

On the other hand, the bi-metallic Cat-1 and Cat-2 exhibit uniquely similar XRD diffractograms (Figure 1) dominated by diffraction peaks ($2\theta = 14.5, 28.1, 38.4, 49.1, 55.4, 64.1, 65.0$ and 72.0°) matching those reported (International Center for Diffraction data, 2018; Wefers & Misra, 1987) for the layer-structured crystalline boehmite (γ -AlO(OH)). According to data reported elsewhere (Wefers & Misra, 1987), this experimental result may mean that the initial γ -Al₂O₃ must have dissolved, at least a good proportion of it, in the strongly acidic medium ($\text{pH} \leq 4$) furnished during the impregnation process of Cu and Zn ions. The heat treatment imposed by the process must have provided an encouraging hydrothermal condition for the precipitation of γ -AlO(OH) (Wefers & Misra, 1987). The fact that the d-spacing (0.599 nm) corresponding to the strongest diffraction peak ($2\theta = 14.5^\circ$) is slightly less than that (0.615 nm) reported for pure γ -AlO(OH) (Wefers & Misra, 1987) may view more closely stacked layers in the boehmite formed in the present catalysts. Intercalary inserted metal ions of the catalysts may explain the closer stacking of atomic layers in the γ -AlO(OH) structure. It is worth noting, however, that the diffractogram still declares the presence of a minor proportion of γ -Al₂O₃ in the catalysts (Cat-1 and Cat-2). This

may reflect that the $\gamma\text{-Al}_2\text{O}_3$ to $\gamma\text{-AlO(OH)}$ conversion process is kinetically controlled under the hydrothermal condition furnished during the impregnation process. It may appear surprising that the also recycled bi-metallic Cat-3 (Table 1) has given rise to a diffraction pattern completely void of the diagnostic peaks of $\gamma\text{-AlO(OH)}$, though a similarly strong acidic medium was furnished. The difference between the metallic constitutions of Cat-3 and the catalysts Cat-1 and -2 lies in its much smaller content of Zn ions (0.03 vs. 4.8%), which may supposedly emphasize the importance of intercalation of Zn ions (rather than Cu ions) to the stabilization of the layer structure of $\gamma\text{-AlO(OH)}$, though Cu^{2+} and Zn^{2+} are of comparable ionic radii, namely 73 vs. 74 pm (Aylward & Findlay, 1994).

Table 2. XRD-determined crystalline phase composition of the recycled and reference catalysts

Catalyst	Phase composition	Abundance	JCPDS ^a
Cat-1/-2	$\gamma\text{-AlO(OH)}$ ^b	Major	83-2384
	$\gamma\text{-Al}_2\text{O}_3$	Minor	29-0063
Cat-3	$\gamma\text{-Al}_2\text{O}_3$	Dominant	29-0063
	$\alpha\text{-Al}_2\text{O}_3$	Trace	85-1337
Cat-4/-5	$\gamma\text{-Al}_2\text{O}_3$	Major	29-0063
	m-CuO ^c	Minor	48-1548
Cat-6/-8/-9	$\alpha\text{-Al}_2\text{O}_3$	Trace	85-1337
	$\gamma\text{-Al}_2\text{O}_3$	Dominant	29-0063
Cat-7/-10	$\gamma\text{-Al}_2\text{O}_3$	Major	29-0063
	$\alpha\text{-Al}_2\text{O}_3$	Minor	85-1337

^a JCPDS card number (International Center for Diffraction data, 2018); ^bBoehmite; ^c m = monoclinic.

3.2 The Catalytic Activity

The activity of the test catalysts in the combustion (total oxidation) of methane (or ethane) was assessed with 1000 ppmv in air as function of the reaction temperature (275-600°C). Experimental data were collected after ensuring the steady state condition at each reaction temperature. Irrespective of the catalyst tested, no conversion of methane (or ethane) species was detectable at < 275°C; it commenced and increased with the reaction temperature ($\geq 275^\circ\text{C}$). On the pure $\gamma\text{-Al}_2\text{O}_3$ (Cat-0), no conversion was observed up to 500°C, and only a negligible conversion ($\leq 2\%$) was observed at 600°C. The light-off temperature (T_{10}) is the minimum temperature at which noticeable conversion occurs, while T_{50} and T_{90} are the temperatures at which 50% and 90% conversion were accomplished. These were readily determined from the conversion-temperature plots compared in Figures 2 and 3 for the combustion of methane or ethane, respectively, and set out, alongside the catalyst specific surface area in Table 3. These results show that on a given catalyst the T_{10} of ethane assumes a lower value than that of methane, thus revealing, expectedly, the more facile oxidation of the former than the later VOC.

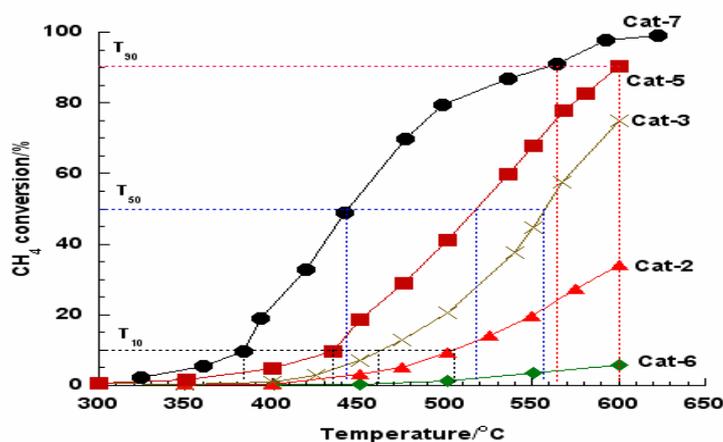


Figure 2. Plots of methane conversion (%) as a function of reaction temperature over the catalysts indicated

Considering the relative performances of the mono-metallic catalysts, the Cu-containing catalysts (Cat-4 and -5) show much higher activity in the oxidation of methane (or ethane) than the Zn-containing Cat-6. In fact, Cat-6 is shown to be the least active relative to all the catalysts tested. The fact that, the mono-metallic catalysts were found to assume similarly high specific surface areas ($S_{\text{BET}} = 104\text{-}107 \text{ m}^2/\text{g}$, Table 3) and that the Zn content (4.6%) is shown not to segregate into XRD-detectable separate phases (Table 2), may help revealing that Cu sites are much more active oxidation centers for methane (or ethane) than Zn sites. There is a consensus that the catalytic oxidation function is more facilitated on strongly basic sites and/or redox sites exposed on the catalysts (Hussein *et al.*, 1991). The former sites ought to be capable of oxidative dehydrogenation (like in the dehydrogenation of alcohols (Hussein *et al.*, 1991)), whereas the latter capable of generating surface electron mobility (like in coupled redox metal sites (Standard electrode potential, 2018). Reported redox potential of $\text{Cu}^{2+}/\text{Cu}^+$ ($= +0.15 \text{ V}$) is much higher than that ($= -1.199 \text{ V}$) of $\text{Zn}^{2+}/\text{Zn}^0$, a fact that accounts for a much more facile electron mobilization in the Cu redox system than in the Zn redox system (Standard electrode potential, 2018).

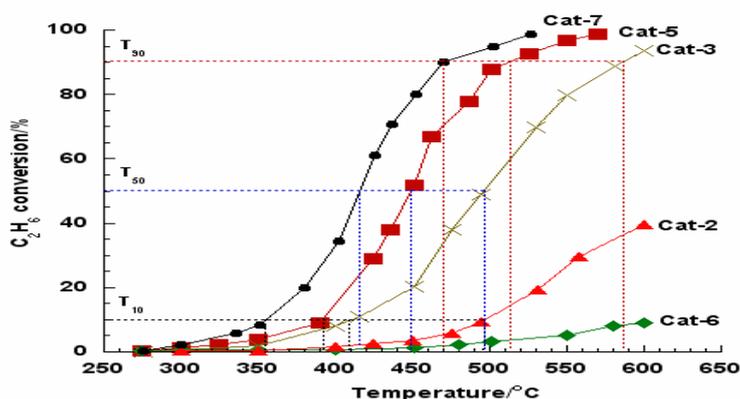


Figure 3. Plots of ethane conversion (%) as a function of reaction temperature over the catalysts indicated

Table 3. Catalyst BET-surface area, and the thereon determined combustion temperatures of methane or ethane in air at 10%, 50% and 90% conversion efficiencies

Catalyst	$S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	Combustion temperature of methane			Combustion temperature of ethane		
		T_{10} /°C	T_{50} /°C	T_{90} /°C	T_{10} /°C	T_{50} /°C	T_{90} /°C
Cat-0 ^a	11.8	n.d. ^b	n.d.	n.d.	n.d.	n.d.	n.d.
Cat-1	107	477	n.d.	n.d.	460	588	n.d.
Cat-2	97	503	n.d.	n.d.	496	n.d.	n.d.
Cat-3	95	461	558	n.d.	410	496	588
Cat-4	104	434	531	600	365	440	513
Cat-5	105	435	518	600	392	450	512
Cat-6	107	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cat-7	105	383	443	565	355	415	470

^aPure $\gamma\text{-Al}_2\text{O}_3$ is coded as Cat-0; ^bn.d = Not determinable

Accordingly, one may explain the much higher oxidation activity of methane (or ethane) observed on Cat-4 and -5 than Cat-6 by the easiness with which the oxidation state of Cu is shuttled between the divalent and mono-valent states and the higher electron mobility thereby facilitated.

The above discussion may still be extended to the Cu-Zn bimetallic Cat-3, which may be considered a quasi-mono-metallic Cu-containing (2.2%) catalyst but with a scarce amount of Zn (0.03%). It is obvious from Figures 2 and 3, and Table 3, that the co-existence of such a minute amount of Zn was sufficient to render Cat-3 detectably less active than the Cu-containing mono-metallic Cat-4 (2.2% Cu). This may presume that the dispersed Zn atoms might have covered up parts of the exposed Cu redox sites. A weaker activity was observed for the reference Cu-Zn bimetallic Cat-8 and -9, which may, thus, be attributed to their higher contents of Zn (2.2%). Whereas the still weaker activity of the recycled Cu-Zn bimetallic Ca-1 and -2 may well be ascribed to the radical

change happened in their phase compositions accompanying the support ($\gamma\text{-Al}_2\text{O}_3$) transformation into the boehmite ($\gamma\text{-AlO(OH)}$) phase (Table 2) as assisted by the inevitably strong acidity ($\text{pH} \leq 4$) of the recovered impregnating solution. Such a radical change might enclose coexisting metal ions (viz., Cu and Zn) leaving behind only low proportions of them exposed on the surface. It is worth noting, that the non-occurrence of such $\gamma\text{-Al}_2\text{O}_3$ to $\gamma\text{-AlO(OH)}$ transformation in the reference Cat-8/-9 was due, most likely, to the failure of their prepared impregnating solution ($\text{pH} = 5.5$) to furnish the strong acidity ($\text{pH} \leq 4$) capable of dissolving the $\gamma\text{-Al}_2\text{O}_3$ support (Table 2). A role for the accompanying loss on the surface area from 118 ($\gamma\text{-Al}_2\text{O}_3$) down to 107 (Cat-1) and further to 97 m^2/g (Cat-2) cannot be excluded with certainty.

The quatro-metallic Cat-7 and Cat-10 are similarly majored by 1.9 %Ni and minored by 0.11% Cu, 0.3% Fe and 0.14% Zn (Table 1), but Cat-7 is recycled and Cat-10 is a reference catalyst. Based on the XRD results (Table 2), the phase composition of both catalysts is also similarly majored by $\gamma\text{-Al}_2\text{O}_3$ and minored by $\alpha\text{-Al}_2\text{O}_3$ with no detectable indication for segregated transition metal oxide phases (Figure 1). Hence, it is legitimate to suggest that oxide species of the four metal ions are highly dispersed on the support. Cat-7 was the catalyst tested in the oxidation reactions of methane (Figure 2) or ethane (Figure 3), and the results obtain reveal its superiority as compared to the other mono- and bimetallic catalysts examined. The results allocate it the lowest light-off temperature value in the oxidation of methane ($T_{10} = 383^\circ\text{C}$) and ethane ($T_{10} = 355^\circ\text{C}$). It is also shown that 90% conversion of methane or ethane was achievable at 565 or 470 $^\circ\text{C}$, respectively. These results reveal that the recycled Cat-7 is more active than the reported Co-Mn (Li *et al.*, 2009) and Co-Cr (Chen *et al.*, 2013) catalysts, for a T_{90} of 320 $^\circ\text{C}$ was determined on the former catalyst, whereas a T_{90} of 464 $^\circ\text{C}$ was determined on the reported catalyst.

The quatro-metallic constitution of Cat-7 may facilitate the availability on the surface not only of Cu redox sites ($\text{Cu}^{2+}/\text{Cu}^{1+}$), but also of Fe ($\text{Fe}^{3+}/\text{Fe}^{2+}$) and Ni ($\text{Ni}^{3+}/\text{Ni}^{2+}$) (Hussein *et al.*, 1991; Nohman *et al.*, 2005; Hasan *et al.*, 1999). To optimize the oxidation activity of Cat-7 (Table 3) these possible redox systems would have somehow cooperated so that the facile reduction of Cu^{2+} -to- Cu^{1+} would compensate for the difficult reduction of Fe^{3+} -to- Fe^{2+} , meanwhile the facile oxidation of Fe^{2+} -to- Fe^{3+} would compensate for the difficult oxidation of Ni^{2+} -to- Ni^{3+} . Hence, Cat-7 assumes a surface exposing more facile electron mobility than the mono-metallic Cat-4 and -5. It is worth noting, in this regard, that the surface areas of Cat-7, Cat-4 and Cat-5 are similarly close to 105 m^2/g . This may help bringing into prominence the important role of the metallic constitution of the catalyst in determining its total oxidation activity.

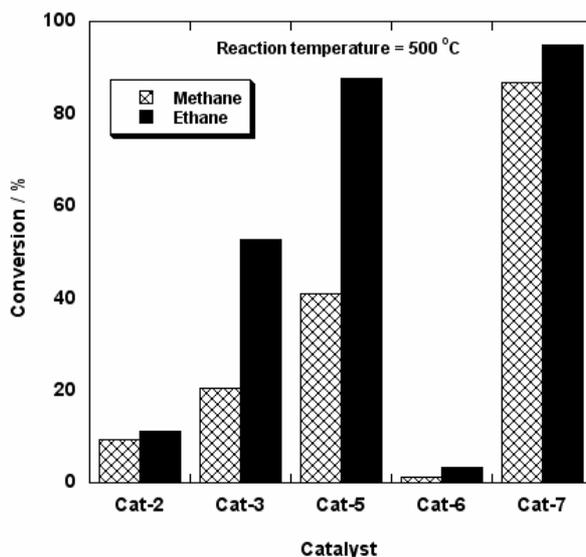


Figure 4. Methane or ethane conversion (%) at 500 $^\circ\text{C}$ as a function of the catalyst used

Summing up, the results of the catalytic activity measurements indicate that (i) the catalytic combustion of ethane is more facile than methane, (ii) the supported metallic constitution on $\gamma\text{-Al}_2\text{O}_3$ is the key parameter in optimizing the oxidation activity of the catalysts, (iii) the test catalysts, whether recycled or reference catalysts, can be arranged in the following activity descending order: Cat-7 > Cat-4/-5 > Cat-3 > Cat-1/-2 > Cat-6 (Figure 4), (iv)

the sole existence (in Cat-4/-5) or co-existence (in Cat-7) of Cu ions is necessary in the makeup of the active metallic constitution of catalysts, (iv) in the contrary, the sole existence (in Cat-6) and co-existence (in Cat-3/-8/-9) of Zn ions is a deactivating parameter, and (v) the support γ -Al₂O₃ phase is instable to the strong acidity (pH \leq 4) of Zn-containing metal ion impregnating solutions made up using acid-leachates of spent catalysts.

4. Conclusions

The results presented and discussed above may help drawing the following conclusions:

1. Inexpensive, γ -alumina supported transition metal oxide catalysts for the combustion of VOCs, particularly methane or ethane, in air can well be recovered from spent commercial catalysts by mineral acid leaching and subsequent support impregnation, drying and calcination.
2. Cu-containing mono- and multi-metallic catalysts are active in the combustion of methane or ethane in air at 275-600°C.
3. With a light-off temperature as low as 355-383°C, and a conversion as high as 90% at 470-565°C, a recycled γ -Al₂O₃-supported quatro-metallic (Cu-Ni-Fe-Zn) catalyst expose surfaces of optimized activity in the combustion of methane or ethane.
4. The catalytic combustion function seems to reside transition metal redox sites (i.e., electronically coupled metal ions of different oxidation states) capable of promoting the necessary electron mobility at the surface.
5. The acidity of the impregnating solutions recovered from spent catalysts must be controlled to pH $>$ 4 otherwise the γ -Al₂O₃ support is transformed into γ -AlO(OH) during the subsequent hydrothermal drying process.

Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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