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CATALYTIC REACTION MECHANISMS

Total Oxidation of Propene and Toluene on Copper/Yttrium Doped Zirconia[1]

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Abstract—The catalytic oxidation of propene and toluene has been investigated on pure ZrO_2, pure Y_2O_3, and ZrO_2 doped with 1, 5, and 10 mol % Y_2O_3 in the presence or absence of copper (0.5, 1, and 5 wt%). A synergetic effect has been detected since ZrO_2 and Y_2O_3 exhibit significantly lower activities than the mixed oxides. The higher surface areas, related to structural change from mononoclinic (ZrO_2) to tetragonal (ZrO_2–Y_2O_3), partly explained the higher activity of ZrO_2–Y_2O_3. However, it has been shown that the number of anionic vacancies, created by the substitution of Zr^{4+} by Y^{3+}, in yttria-stabilized zirconia solids depends on the yttrium contents. Their effect on propene and toluene oxidation activity is significant. The anionic vacancies should induce better activity of the ZrO_2—5 mol % Y_2O_3 catalyst with or without copper, which presents the higher number of Zr^{3+} species. This support should favor the formation of CuO particles, which should be the most active catalytic sites in the studied reaction.

1. INTRODUCTION

Volatile Organic Compounds (VOCs) are among the main pollutants in the low atmosphere of cities and their release has begun to be severely regulated. In compliance with the stringent environmental regulations, catalytic oxidation can effectively destroy VOC at much lower temperatures than thermal oxidation. The practical applications of the catalytic oxidation process require heating large amounts of gas containing low concentrations of VOCs to find the oxidation temperature. Therefore, highly active catalysts are required at low temperatures. Supported precious metals such as Pt and Pd are well established as efficient catalysts for VOCs combustion [1, 2]. However, for obvious reasons, cheaper catalytic materials, involving base metal oxides, are of ever increasing importance. The use of zirconia as an oxidation catalyst has been claimed by different authors [3, 4] for its thermal stability and specific area. Moreover, the thermal stability and catalytic properties could be enhanced by adding some dopants (Si, La, Ca, Y, Ce…) that change the structure of zirconia [5]. It is known that at low temperatures, ZrO_2 can be stabilized in a tetragonal or distorted cubic phase by adding these dopants [6]. These can be the oxides of metals having their own fluorite like crystallographic lattice and capable of forming solid solutions with zirconia. It was found that the best doping oxide for the stabilization of the fluorite structure is a yttrium oxide. The introduction of yttrium into the zirconia induces the formation of anionic vacancies [7], which increase the ability of the solid to accumulate oxygen and improve the oxygen exchange at low temperature [8]. Moreover, it was found that the ionic conductibility reaches a maximum between 1 and 10 mol % of Y_2O_3 in ZrO_2 [9]. This result could be certainly correlated with the number of anionic vacancies.

The presence of copper in catalysts increases the activity of oxidation reactions [7, 10]. Indeed, among the activity of the following metals (Cu, Mn, Fe, V, Mo, Co, Ni, Zn) for the complete oxidation of toluene, copper was found to be the most promising catalyst [11, 12].

In this paper, propene and toluene have been chosen as probe molecules because of their common emission in industrial processes and because alkenes and aromatics (with carbonyl compounds) are the major families in automobile exhausts [13], especially in diesel engines.

The objective of this work is to investigate the influence of copper and yttrium on the activity and selectivity of zirconia in propene and toluene total oxidation. A reaction mechanism involving the anionic vacancies is also presented. For the impregnated copper samples, the determination of the most active sites is investigated.

2. EXPERIMENTAL

Pure ZrO_2, pure Y_2O_3, and ZrO_2 doped with 1, 5 and 10 mol % Y_2O_3 (respectively Zr1Y, Zr5Y, and Zr10Y) were synthesized by precipitation or coprecipitation of their respective hydroxides ($ZrOCl_2 \cdot 8H_2O$: Acrõs, >98%; $Y(NO_3)_3 \cdot 6H_2O$: Acrõs, >99.9%) at pH ≥ 10 controlled with NH_3 solution followed by calcination under

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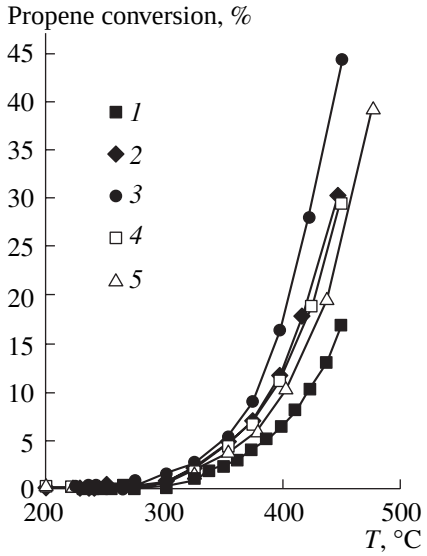

Fig. 1. Propene conversion versus reaction temperature on pure oxide catalysts. (*1*) ZrO_2, (*2*) Zr1Y, (*3*) Zr5Y, (*4*) Zr10Y, (*5*) Y_2O_3.

air flow at 600°C (2°C min^{-1}, 4 h). Impregnation of $Cu(NO_3)_2$ solution ($Cu(NO_3)_2 \cdot 3H_2O$: Prolabo, >99%) was achieved on those oxides to yield an equivalent Cu content of 0.5, 1, and 5 wt%. Impregnated catalysts calcined at 450°C are called, respectively, 0.5, 1, and 5% Cu/support.

Propene oxidation was carried out in a flow microreactor and studied between 25 and 450°C. The flow of reactant gases, air (99 ml min^{-1}), and C_3H_6 (2.3 ml min^{-1}) were adjusted by mass flow controllers. The analysis of combustion products was performed evaluating the propene conversion and the $CO/(CO + CO_2)$ molar ratio from a Varian 3600 chromatograph equipped with TCD and FID. Toluene oxidation was carried out in the same type of catalytic test, but the toluene (2.6 ml gaseous toluene min^{-1}) was mixed in a flash-injector with a flow of air (99 ml min^{-1}) adjusted by a mass flow controller. Before the catalytic tests, the samples (200 mg) were calcined under a flow of air (2 l h^{-1}) at 450°C (2°C min^{-1}) for 4 h. The space velocity was about 40 000 h^{-1} for both reactions. The specific areas of solids are determined by the BET method using a Quantasorb Junior apparatus, and the gas adsorbed at –196°C is pure nitrogen. The Raman spectra were recorded using a Dilor XY monochromator with subtractive dispersion. The samples were excited using 632.8 nm radiation of a He–Ne laser. The electron paramagnetic resonance (EPR) measurements are performed at 20°C and –196°C on an EMX Brüker spectrometer. A cavity operating with a frequency of 9.3 GHz (X-band) is used. The magnetic field is modulated at 100 kHz. Precise g values are determined from simultaneous precise frequency and magnetic field values. X-ray Photoelectron Spectroscopy (XPS) measurements are carried out on all the samples without copper and on the mixed oxides containing 5 wt% of copper. XPS spectra of the catalyst samples were recorded using a Leybold Heraeus LHS 10 instrument (anode operated at 13 kV and 20 mA with fixed analyser transmission mode E_0 = 50 eV applied) equipped with a magnesium anode ($h\nu$ = 1253.6 eV). The samples were deposited on an indium support and the working pressure in the analysis chamber was maintained at 4×10^{-8} mbar. Charging effects were corrected using Zr 3*d* peak at binding energy of 182 eV. The reproducibility of the peak position was estimated to be ±0.2 eV. Surface atomic ratios were obtained on the basis of the peak area intensities after correction of instrumental parameters, photoionization cross sections, and electron mean free paths.

3. RESULTS AND DISCUSSION

3.1. Study of the Support Oxides for Propene and Toluene Oxidation

The behavior of the different oxides for the propene oxidation is described in Fig. 1. The activity of pure Y_2O_3 is more important than that of pure ZrO_2. This result is emphasized since the surface area for Y_2O_3 is lower than that for ZrO_2. At 425°C, oxidation of C_3H_6 is only about 10% for pure zirconia and more than 20% for the yttrium doped zirconia. Nevertheless, we observed that an addition of 1% yttrium in the structure of the zirconia is enough to increase the activity of the catalyst. This effect can be explained by the modification of the zirconia structure when yttrium is added.

The XRD study obtained during the calcination of $ZrO(OH)_2$ shows the tetragonal phase formation up to 700°C. After cooling from 700 to 27°C under a flow of air, the transformation of the part of the tetragonal phase into the monoclinic one took place. This result can explain the 18 Raman active modes (characteristic of monoclinic phase) observed at room temperature for ZrO_2 (after calcination and cooling). The tetragonal phase was stabilized in the Zr1Y, Zr5Y, and Zr10Y samples since, for the latter, the Raman spectra revealed five Raman active modes characteristic of tetragonal phase.

The stabilization of the tetragonal structure of ZrO_2 by adding yttrium also induces a beneficial effect on the specific area since a significant increase of the BET area (from 70 to 95 m^2/g) is observed for Zr1Y, Zr5Y, and ZrlOY samples.

However, among the stabilized zirconia, Zr5Y catalyst presents a better catalytic behavior. An explanation could be given taking into account the EPR measurements of oxides before and after the catalytic test. The Zr^{3+} cations (signals with $g_\perp$ = 1.977 and $g_\parallel$ = 1.959) were evidenced in the solids [14–15]. The origin of Zr^{3+} ions has been already discussed [14, 16]. Indeed, during the calcination of $ZrO(OH)_2$ into ZrO_2, the OH groups were responsible for the reduction of Zr^{4+} into Zr^{3+} ions. At higher temperatures, the reduction of Zr^{4+} by the trapped single electrons in the solids could occur. Fig. 2, *1* displays the number of Zr^{3+} species before the

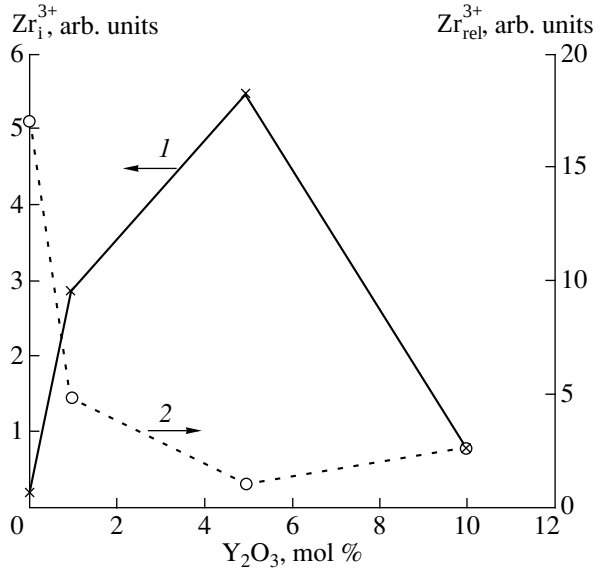

Fig. 2. (*1*) Initial number of Zr^{3+} species (Zr_i^{3+}) and (*2*) ratio of number of Zr^{3+} species after and before the catalytic test (Zr_{rel}^{3+}) versus yttrium content in ZrO_2.

catalytic test (Zr_i^{3+}) versus yttrium in the different solids. We found that the concentration of Zr^{3+} in the ZrO_2–Y_2O_3 was much more than in ZrO_2, especially, when we doped zirconia with 5 mol % Y_2O_3 (see Fig. 2, *1*). The increasing Zr^{3+} concentration in the order ZrO_2 < Zr10Y < Zr1Y < Zr5Y can be related to increasing anionic vacancy concentrations. Indeed this result can be correlated with the ionic conductibility which reaches a maximum between 1 and 10 mol % Y_2O_3 in ZrO_2 [9]. Moreover, O_2^- anion radicals are considered by many investigators as intermediate species in the catalytic oxidation on the solid surfaces. Markaryan *et al.* [17] have shown that yttrium introduction in CeO_2–ZrO_2 solid solutions leads to more reactive O_2^- anion radicals in correlation with the number of anionic vacancies. According to this conclusion, the best activity of Zr5Y could be explained by the higher oxygen vacancies.

The oxidation mechanism implies the intervention of chemisorbed activated oxygen [18]. On zirconia, the formation of this anionic oxygen species (O_{2ads}^-) could be explained by the intervention of Zr^{3+} species and anionic vacancies (□) by the following mechanisms:

$$1)\ Zr^{3+}, \square_{surf} + O_2 \longrightarrow Zr^{4+}, \square_{surf}\text{–}O_2^-,$$

$$2)\ Zr^{4+}, \square_{surf}\text{–}O_2^- + CH_2\text{=}CH\text{–}CH_3$$

$$\longrightarrow Zr^{4+}, \square_{surf}\text{–}O_2^-\text{–}CH_2\text{–}\dot{C}H\text{–}CH_3,$$

$$3)\ Zr^{4+}, \square_{surf}\text{–}O_2^-\text{–}CH_2\text{–}\dot{C}H\text{–}CH_3 + \text{oxygen}$$

$$\longrightarrow Zr^{3+}, \square_{surf} + \text{products}.$$

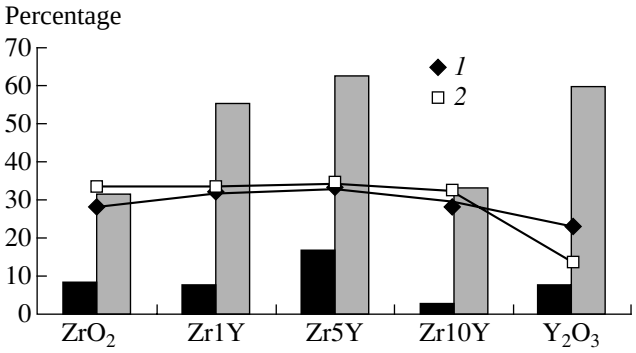

Fig. 3. Total oxidation of toluene on the supports. Black histogram: % conversion at 400°C, Grey histogram: % conversion at 450°C, (*1*) %CO at 400°C, (*2*) %CO at 450°C.

The ratio of the content of Zr^{3+} cations after the catalytic experiments to their initial content (Zr_{rel}^{3+}) was minimal (~1) for the Zr5Y sample (Fig. 2, curve *2*), which points to a higher stability of this catalyst in the catalytic experiments. The increase in the concentration of Zr^{3+} ions in the Zr1Y, Zr10Y, and ZrO_2 samples after the oxidation can be due to the reduction of Zr^{4+} ions by propylene.

As the only carbonaceous products are CO and CO_2, another result must be underlined concerning the CO selectivity. Whatever the mixed oxide used, the CO selectivity is around 60 to 70%, which seems to be a compromise between those for ZrO_2 and Y_2O_3.

The behavior of the different oxides at 400 and 450°C for the toluene oxidation is described in Fig. 3. The oxidation of toluene can be measured only after a reaction temperature of 350°C, compared with 250°C for propene oxidation. As for propene oxidation, the Zr5Y catalyst displays the highest activity. However, a reaction temperature of 450°C is never sufficient to oxidize all the toluene. Yttrium oxide catalyst is better for toluene oxidation than zirconia as the conversion at 400°C is similar for both solids but the activity for Y_2O_3 is twice that for ZrO_2 at 450°C. Addition of 1% of yttrium in the structure of zirconia is enough to increase the activity of the catalyst but for high yttrium content (10 wt %) the promotional effect disappears as the activity of Zr10Y and ZrO_2 are quite the same.

—Zr5Y catalyst which presents a singular catalytic behavior for the toluene oxidation could be related to Zr^{3+} ion concentrations and connected to increasing anionic vacancy concentrations as for the propene oxidation.

—The only products are CO, CO_2, and water. Concerning the CO selectivity (Fig. 3), whatever the mixed oxide or zirconia used, the selectivity is around 35% and there is a low increase from 400 to 450°C. The CO selectivity for Y_2O_3 is slightly lower at 400°C (~23%) and decreases at higher temperature (13% at 450°C).

The Zr5Y sample is the most active catalyst in both oxidation reactions. The higher activity of Zr5Y could

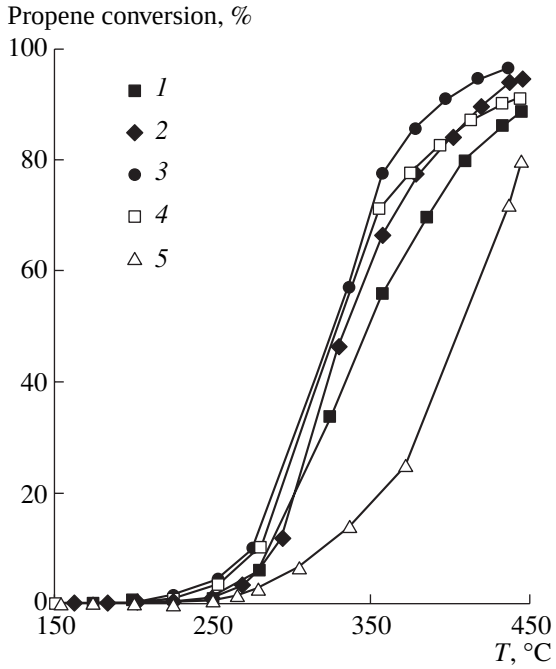

Fig. 4. Propene conversion versus temperature on copper supported (0.5 wt%) catalysts. (*1*) 0.5%Cu/ZrO_2, (*2*) 0.5%Cu/Zr1Y, (*3*) 0.5%Cu/Zr5Y, (*4*) 0.5%Cu/Zr10Y, (*5*) 0.5%Cu/Y_2O_3.

be explained by the higher number of oxygen vacancies (more Zr^{3+}) in the sample. Moreover, total oxidation is never achieved below 450°C. Regardless, these systems possess high selectivity for CO (especially for propene oxidation).

For environmental applications, the Zr5Y catalyst could not be used directly for VOC oxidation.

3.2. Study of Impregnated Copper Oxides for Propene and Toluene Oxidation

Copper impregnation implies a promotional effect for the propene conversion and the inhibition of CO formation in favor of CO_2. Therefore, the CO_2 selectivity is 100% for the carbonaceous products. This characteristic effect of copper is well known [11, 12] and explains why the light off of CO oxidation for copper deposed on yttria-stabilized zirconia is so improved [19].

Binding energy of Cu 2*p*3/2 core level of 5%Cu/mixed oxides catalysts and the corresponding Cu/Zr surface molar ratio

Catalyst	Binding energy of Cu 2*p*3/2, eV	Cu/Zr molar ratio
Cu/Zr1Y	934.1	0.40
Cu/Zr5Y	933.6	0.45
Cu/Zr10Y	934.0	0.30

Figure 4 illustrates the evolution of support effect on the activity of propene conversion on 0.5 wt % impregnated catalysts. We observe that conversion always begins at about 250°C whatever the Cu content. However, the propene conversion at higher temperatures shows the important effect of the support. According to the specific areas, the following activity order was obtained: $Cu/Y_2O_3 < Cu/ZrO_2 < Cu/ZrO_2–Y_2O_3$. This result could be explained by a better dispersion of copper at higher specific surfaces. Nevertheless, among all the samples doped with copper, Cu/Zr5Y gave the best activity. The investigation of copper species nature (type of copper, valence, environment…) of our supported solids is then important to understand the catalytic activities.

Studying the Cu2*p*3/2 XPS core level in all the samples, the presence of a satellite peak close to the principal one unambiguously indicates copper +II at the surface [20]. Moreover, the spectral parameter, that is the ratio of the intensities of the satellite (I_{sat}) and the principal (I_{pp}) peaks composing the Cu 2*p*3/2 line, would be an indicator of the distribution of copper(II) ions in the tetrahedral and/or octahedral sites of the structure. The I_{sat}/I_{pp} value (0.60) obtained on the different compounds indicates that Cu^{2+} ions are in octahedral symmetry surrounded by less than six ligands (between five and six) of O^{2-} ions. These results are close to that obtained by EPR measurements where $A_{\|}$ = 134 G signify a number of ligands less than 6 in an octahedral symmetry.

In addition, the XPS results are close to those obtained on bulk CuO [20–21], thus proving that the surface of the impregnated catalyst may be composed of CuO phase. This assertion is strengthened by the Cu2*p*3/2 (934 eV for CuO [22–23]) binding (energy on Cu/Zr1Y and Cu/Zr10Y, 934.1 and 934.0 eV, respectively (table). However, a significant shift in the binding energy (933.6 eV) is observed for Cu/Zr5Y (table) indicating a more reduced copper environment for this sample. The higher quantity of Zr^{3+} in Zr5Y should induce this reducing environment. Moreover, studying the surface composition (Cu/Zr atomic ratio) for all the samples, a copper surface enrichment is observed (table) but is more pronounced for Cu/Zr5Y : 0.40, 0.45, and 0.30 for respectively Cu/Zr1Y, Cu/Zr5Y, and Cu/Zr10Y. CuO in a more reducing environment and a higher surface copper enrichment is then observed for the Cu/Zr5Y sample.

The Cu^{2+} environment modifications could be evidenced by EPR technique. The EPR spectrum of copper is composed of two signals. The first one with an axial symmetry is well resolved in its hyperfine structure ($A_{\|}$ = 134 G, $g_{\|}$ = 2.34 and $g_{\perp}$ = 2.069, g_{iso} = 2.15). This signal is characteristic of isolated Cu^{2+} ions (I = 3/2) located on catalyst surfaces with octahedral symmetries. The second one is a broad and isotropic signal centered at g_{iso} = 2.15 with ΔH = 265 G and could unambiguously be attributed to Cu^{2+} clusters present in the solid. These two kinds of Cu^{2+} species having the

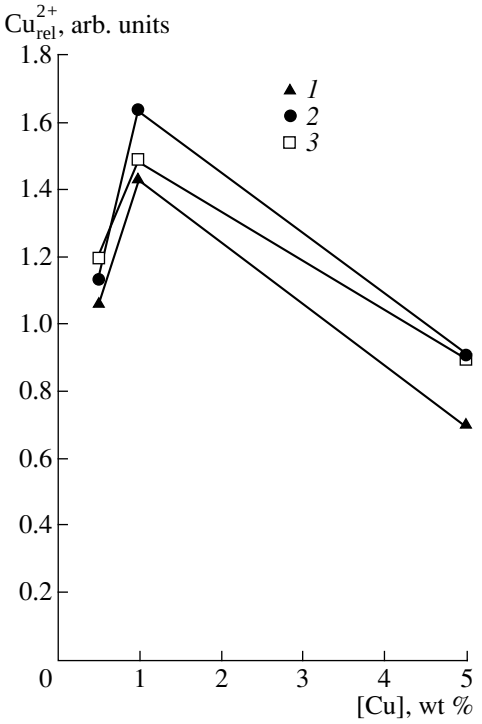

Fig. 5. Dependence of Cu^{2+}_{rel} on the concentration of copper in the various Cu/Zr-Y catalysts. (*1*) Zr5Y, (*2*) Zr1Y, (*3*) Zr10Y.

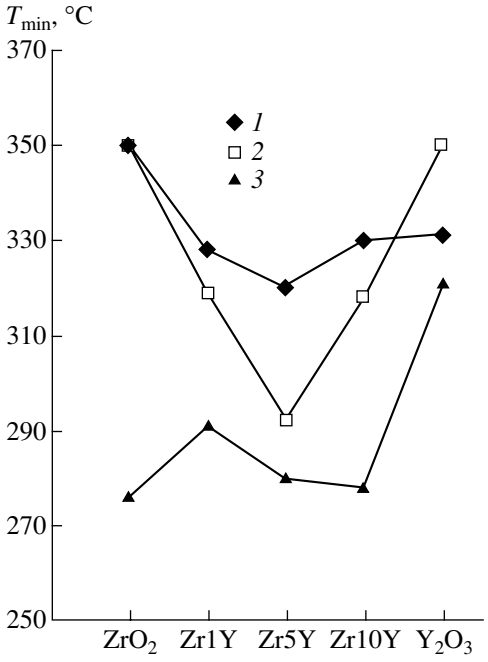

Fig. 6. Total oxidation of toluene on the copper based catalysts. (*1*) 0.5%Cu, (*2*) 1%Cu, (*3*) 5%Cu.

same g_{iso} value indicate that they are located in the same sites. The relative amounts of Cu^{2+} (Cu^{2+}_{rel}) in our samples are reported in Fig. 5. For the same support, when increasing copper content from 0.5 to 1%, the relative number of Cu^{2+} ions increases. Moreover, this number for 1% copper content is not double that for 0.5% copper content, meaning that there is formation of CuO particles, which is not detectable by EPR. In addition, the decrease of the Cu^{2+} relative number for 5% copper content means an increase in CuO formation.

The relative number of Cu^{2+} ions remains the same for all the samples after the catalytic tests, which might signify that particles of CuO are the main active species, rather than isolated Cu^{2+} and clusters, for both oxidation reactions.

On the other hand, we can compare the relative number of Cu^{2+} species for the same copper content on the different Zr–Y supports because of their similar densities. It is noted that 0.5%Cu/Zr-5Y has the lowest relative number of Cu^{2+} species compared to 0.5%Cu/Zr-1Y and 0.5%Cu/Zr-10Y. Since these mixed supports have similar surface areas, it is assumed that the best activity of 0.5%Cu/Zr-5Y could be due to its highest tendency to form small particles of CuO.

Therefore, the stabilization of more reduced copper could partly explain the superior activity of Cu/Zr5Y in propene oxidation. Actually, Jerhigan and Somorjai [24] have shown that the more the copper is reduced the more the activity is for total oxidation reactions, whereas Centi *et al.* [25] have indicated that the reducibility of copper increases on ZSM-5 or ZrO_2 (especially on tetragonal phase of ZrO_2). Moreover, we might deduce that the higher anionic vacancies on Zr5Y support could directly explain its higher activity, noting also that Dow *et al.* [7, 26] have shown that copper atoms can occupy the anionic vacancies leading to a stable interfacial Cu_2O formation. However, XPS measurements have proved the presence of CuO phase and the absence of Cu_2O. This result is in accordance with those of Indovina *et al.* [27] showing that the calcination of zirconia samples prepared from Cu-nitrate should cause no copper reduction, but in our case the CuO particles are in a more reductive environment for the 5%Cu/Zr5Y. Moreover, this sample also presents a higher surface quantity of copper. This result should be correlated to EPR measurements which show that the higher quantity of Cu^{2+} ions and clusters (partly located in the bulk) are observed on the Cu/Zr1Y and Cu/Zr10Y samples whereas the higher quantity of surface CuO particles are found for Cu/Zr5Y.

The higher activity of the Cu/Zr5Y sample for propene oxidation could be due to its having the highest tendency to form active particles of CuO in a more reducing environment.

The catalytic behavior of these solids for propene oxidation can be extended for toluene degradation. In fact, the promotional effect of copper could be also observed on Fig. 6 for total conversion of toluene on the different copper supported catalysts. The inhibition of

CO formation in favor of CO_2 (S_{CO_2} = 100%) when copper is present on the catalyst is observed too. The activity is emphasized since the curves are shifted to lower minimal temperatures with increasing copper content from 0.5 to 5 wt %. For example, the minimal temperature for the total conversion of toluene in Zr5Y samples with copper content of 0.5, 1, and 5 wt % decreases gradually from 320 to 290, then to 280°C, respectively. This good catalytic potential can be directly compared with the minimal temperature for total conversion of toluene on 5 wt % $Cu/\gamma Al_2O_3$ and 5 wt % Cu/NaHY catalysts which are at about 320 and 340°C, respectively [11, 12] in similar conditions. Moreover, 0.5% of supported copper is enough to obtain total conversion under 350°C whatever the catalyst used. The catalysts impregnated with 0.5 and 1 wt % of copper presented almost the same catalytic behavior as for propene oxidation and Zr5Y was the best catalyst. For the solids with 5 wt % of loaded copper, the catalytic tendency was less pronounced and their catalytic behavior were similar (except for the lower activity of 5 wt % Cu/Y_2O_3). This could be due to a lower effect of the support oh the CuO particles when the impregnated copper is over 1 wt %.

The same behavior is then obtained for both the studied oxidation reactions:

—Total oxidation was then always achieved under 350°C and the copper induces the inhibition of CO formation in favor of CO_2;

—The Zr5Y sample is also the more active catalyst with impregnated copper. The best activity of Cu/Zr5Y could be explained by a higher quantity of CuO particles in a more reducing environment.

Therefore, the Cu–O bond should be slightly weaker in this last sample, and then oxygen should be more easily removable. The redox cycle mechanism for CuO is generally given in two steps [28]:

$$\mathrm{VOC} + \mathrm{O_{SL(CuO)}} \longrightarrow \text{products } (\mathrm{CO_2} \text{ and } \mathrm{H_2O}) + \square_{\mathrm{S(CuO)}}, \quad \text{(I)}$$

$$\mathrm{O_2} + 2\square_{\mathrm{S(CuO)}} \longrightarrow 2\mathrm{O_{SL(CuO)}} \quad \text{(II)}$$

with: $O_{SL(CuO)}$: surface lattice oxygen of CuO;

$\square_{S(CuO)}$: surface oxygen vacancy of CuO.

In our case, the step (I) should be facilitated by the higher reducibility of CuO particles in interaction with the anionic vacancies of the support.

Moreover, the step (II) should be also fastened by anionic vacancies of the support, which are suitable sites for oxygen adsorption leading to easier formation of atomic-type oxygen species than on CuO.

Thanks to the oxygen-ion conducting ZrY, the step (II) could be modified by the use of anionic vacancies of the support ($\square_{S(Zr)}$):

$$\mathrm{O_2} + 2\square_{\mathrm{S(Zr)}} \longrightarrow 2\mathrm{O_{SL(Zr)}}, \quad \text{(III)}$$

$$2\square_{\mathrm{S(CuO)}} + 2\mathrm{O_{SL(Zr)}} \longrightarrow 2\mathrm{O_{SL(CuO)}} + 2\square_{\mathrm{S(Zr)}}. \quad \text{(IV)}$$

Therefore the highly active and selective Cu/Zr5Y catalyst for VOC oxidation could be explained by the synergetic effect between CuO particles and vacancies of ZrY.

4. CONCLUSION

In this work, the catalytic activity for oxidation of propene and toluene was found to increase for the studied catalysts in the following order: $ZrO_2 < Y_2O_3$, Zr10Y, Zr1Y < Zr5Y < Cu/Y_2O_3 < Cu/ZrO_2 < Cu/Zr10Y, Cu/Zr1Y < Cu/Zr5Y. BET measurements could partly explain this order since the surface area of pure zirconia is only 70 m^2/g whereas it is about 93 m^2/g for ZrY samples. The increase of surface area was explained by the structural phases change, addition of yttrium to zirconia (monoclinic) leading to the stabilization of the tetragonal phase (Raman characterization). However, another explanation could be given taking into account the EPR measurements of oxides before and after the catalytic test. At high temperatures, the reduction of Zr^{4+} by the trapped single electrons in the solids could occur. The increasing Zr^{3+} concentration in the order ZrO_2 < Zr10Y < Zr1Y < Zr5Y can be connected to increasing anionic vacancy concentrations. The best activity of Zr5Y could then be explained by higher oxygen vacancies and an oxidation mechanism for propene oxidation was proposed. Moreover, the higher quantity of vacancies observed for ZrO_2–5 mol % Y_2O_3 induces the better activity of this catalyst whether impregnated with copper or not. In the absence of copper, its catalytic potential for VOCs oxidation is not enough because total conversion was never achieved under 450°C and CO formation is too important. However, whatever the support, copper has a promotional effect on the activity and leads to an inhibition of CO formation in favor of CO_2. Oxygen vacancies and the structure of the support would induce the higher formation of active CuO particles in a reducing environment. The samples Cu/Zr5Y are then the best studied catalysts and are powerful catalysts for propene and toluene oxidations.

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