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ARTICLE

Catalytic Wet-Air Oxidation of *p*-Cresol on $Ag/Al_2O_3-ZrO_2$ Catalysts

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ABSTRACT: Catalytic wet-air oxidation of *p*-cresol was carried out on $Ag/Al_2O_3-ZrO_2$ catalysts at 1, 5, 10, and 20 wt % of ZrO_2 in a reactor-type batch and 160 °C and 15 bar of oxygen. $Al_2O_3-ZrO_2$ supports were prepared by the simultaneous hydrolysis of the boehmite and zirconium alkoxide. $Ag/Al_2O_3-ZrO_2$ catalysts prepared by deposition−precipitation showed higher surface area (202−216 m^2/g) and lower Lewis acids sites than the Ag/Al_2O_3 (161 m^2/g) and Ag/ZrO_2 (25 m^2/g) reference catalysts. FTIR-CO adsorption showed a shift to lower frequencies on $Ag/Al_2O_3-ZrO_2$ catalyst indicating electron-rich metallic particles. The *p*-cresol conversion, TOC abatement, and CO_2 selectivity were improved when Ag was supported on $Al_2O_3-ZrO_2$ mixed oxides. A modification of the surface properties of Ag on the $Ag/Al_2O_3-ZrO_2$ catalysts due to a metal−support interaction leading to a faster oxidation of the adsorbed reactant species is proposed.

INTRODUCTION

Phenols are environmental pollutants present in discharge wastewaters from fossil fuel refining processes, phenol manufacturing plants, and a variety of industries. These phenolic compounds are toxic and nonbiodegradable by conventional methods, and the U.S. Resource Conservation and Recovery Act (RCRA), classifies the effluents containing phenols as highly dangerous.[1,2] Processes such as the catalytic wet advanced oxidation route (CWAO) are favorable for converting the organic pollutants matter into carbon dioxide and water.[3−6] In this way, metallic oxides like CuO have been successfully used as catalyst for the degradation of phenols (phenol, cresols, chlorophenols, nitrophenols, etc.) via CWAO.[7,8] A combination of various metallic oxides as CuO−ZnO supported on alumina,[9] CeO_2, or CeO_2 promoted with CuO and MnO, and noble metals as Rh and Pt have also been reported as good alternative catalysts for phenols degradation.[10−14]

Catalytic wet-air oxidation on carbon support[15] as well as transition metals oxides as FeO, Co_2O_3, NiO, and CuO provide efficient methods[16] for phenol degradation. Support effects on noble metals were observed for CWAO of phenol; thus the support stabilizes the metallic surface area of Ru, Rh, Pt, Pd, Ag, and Au noble metals when they are supported on Al_2O_3, SiO_2, or TiO_2. The support provides high dispersion, enhanced activity, and stability[4,6,16−21] to the active metal.

Zirconia, as a support, has also been used for the CWAO process in which Kraft-bleaching wastewater is successfully treated using Ru-supported on ZrO_2. However, zirconia has the disadvantage of having a very poor area.[22] This takes into account that zirconia can be a good support for the CWAO process. In the present work the preparation of alternative supports for noble metals involving zirconium oxide was studied in the CWAO of *p*-cresol. Specifically, the catalytic wet-air oxidation of *p*-cresol, using silver supported on $Al_2O_3-ZrO_2$ mixed oxides (1, 5, 10, and 20 wt % ZrO_2) is reported. The characterization of the mixed oxides was made by means of nitrogen adsorption, XRD, H_2-TPR, FTIR-pyridine adsorption, and FTIR-CO chemisorption.

EXPERIMENTAL SECTION

The $Al_2O_3-ZrO_2$ mixed oxides were prepared at different contents of ZrO_2 (0, 1, 5, 10, 20 wt %) by means of a method that was named "boehmite peptization". The method consists of the addition of a metallic aloxide to the boehmite contained in an acid solution. The peptization of the boehmite and the alkoxide hydrolysis occurs simultaneously. With this method a strong interaction of the alkoxide with the Al−OH groups of the peptized boehmite is obtained, causing a high dispersion of ZrO_2 on the surface of alumina.

Supports and Catalysts Preparation. The γ-Al_2O_3 support was obtained by calcination of boehmite (CONDEA, high purity 99.999%, 74% AlOOH, 26% H_2O) under air flow (3.6 L/min) at 650 °C for 12 h.

$Al_2O_3-ZrO_2$ supports were prepared by boehmite peptization as follows: Catapal boehmita was put in contact with a solution containing 100 mL of butyl alcohol and the water stoichiometrically required to hydrolyze the zirconium alkoxide (Stream Chemicals 98%). For boehmite peptization the pH of the suspension was adjusted with nitric acid to a value of 3; afterward the temperature was increased to 80 °C under agitation for 12 h. Then the suspension was cooled down to room temperature, and the solution containing the $Zr(OC_4H_9)_4$ was added drop by drop in adequate amounts to obtain 0, 1, 5, 10, and 20 wt % of ZrO_2 in the $Al_2O_3-ZrO_2$ mixed oxides. The formation of the mixed oxide was then obtained by increasing the temperature to 100 °C under vigorous agitation and reflux, during 12 h. Afterward, the solids were dried in vacuum until dryness. Finally the solids were maintained in an oven at 120 °C for 12 h and then calcined under air flow at 650 °C for 6 h (60 mL min^{-1}).

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$Ag/Al_2O_3-ZrO_2$ catalysts preparation was carried out by deposition−precipitation (2 wt % Ag nominal). The support was put in contact with a solution of $AgNO_3$ at a concentration of 2.35×10^{-2} M. Then the pH was fitted to 6.8 by the addition of a KOH solution (0.1 and 0.01 M) to precipitate the Ag^+ ions on the support.[23] The suspension was heated up then to 80 °C and kept under vigorous agitation, for 8 h. Afterward the solids were separated by filtration, and then washed with 100 mL of distilled water. This operation was repeated four times. Then, the solids were dried to 120 °C overnight and calcined at 300 °C under air flow for 4 h. Finally, the catalysts were reduced under hydrogen flow at 300 °C for 4 h; afterward, the samples were stored in a desiccator with vacuum. For identification, samples were labeled as $Al_2O_3-ZrO_2X$ (where X represents the weight % of the ZrO_2).

Characterization. The specific surface area of the supports was determined from the nitrogen adsorption isotherms (Brunauer−Emmett−Teller (BET) method) using a Quantachrome Autosorb-3B equipment. Pore mean size diameter distribution was determined from the desorption isotherms and calculated by means of the Barret−Joyner−Halenda (BJH) method.

The X-rays diffraction pattern of the γ-Al_2O_3, γ-$Al_2O_3-ZrO_2$, and ZrO_2 supports were obtained with a SIEMENS D-500 diffractometer with anode of Cu and monocromador of secondary beam. The identification of the compounds was made using the JCPS reference cards 10-0425, 14-0534 D, and 7-0343 corresponding to γ-Al_2O_3 and ZrO_2 crystalline phases, respectively.

The type and amount of acid sites (Brönsted and/or Lewis) on the supports were determined by pyridine adsorption infrared spectroscopy (FTIR) study using a Nicolet 170 SX instrument with Fourier transformation. The solid material was pressed into thin self-supported wafers. Then, they were placed in a glass Pyrex cell with CF_2 windows coupled to a vacuum line, in order to be evacuated (1×10^{-6}) in situ at 400 °C for 30 min. The pyridine adsorption was carried out in the cell at 25 °C. Afterward the adsorbed pyridine was desorbed with vacuum from room temperature to 400 °C on intervals of 100 °C. The quantities of the remaining adsorbed pyridine were obtained from the integrated absorbance bands, following the procedure and using the extinction coefficient reported elsewhere.[24]

H_2-TPR experiments were made in a CHEMBET-3000 (QUANTACHROME Co) equipment using 0.2 g of catalyst by means of the following protocol: samples were heated at 300 °C under nitrogen flow (10 mL min^{-1}) during 30 min. Then, the samples were cooled down to room temperature. A mixed gas flow (5% H_2/95% N_2) was passed then through the cell. The TPR profiles were registered using a heating program of 10 °C min^{-1} from room temperature to 700 °C using a flow rate of the gas mixture of 10 mL/min.

The CO chemisorbed FTIR spectra were obtained at room temperature using a Nicolet-FX710 apparatus. The samples pressed in thin wafers were placed in a Pyrex glass cell equipped with CaF_2 windows. The samples were pretreated *in situ* under hydrogen flow at 300 °C for 30 min, then the samples were cooled down to room temperature and a N_2 flow was passed through the samples during 30 min, after CO was introduced to the system for 30 min and then the FTIR spectra were registered.

The oxidation reactions were performed in a 500 mL batch reactor of stainless steel high-pressure (Parr Instrument Co Ltd., IL) coated with a glass linear to prevent corrosion problems. The reactor includes a stirrer, gas supply system, and temperature controller. In a typical experiment, the reactor was loaded with 300 mL of a solution containing 1000 ppm of *p*-cresol and 1 g/L of catalyst. The system was then heated to the reaction temperature and pressurized with air under continuous stirring of 750 rpm. Time zero was defined when the preset conditions were attained (temperature, 160 °C; oxygen pressure, 15 bar). Periodically, at time intervals of 15 min, samples (10 mL) were withdrawn from the reactor using the sampler valve and analyzed by gas chromatography on a capillary column DB-WAX, 30 m, 0.53(ID), 1.0 μm of film. During the chromatographic analysis 4-methylcatechol, 4-hydroxybenzaldehyde, and 4-hydroxybenzylalcohol were identified.

To complete the carbon balance, total organic carbon (TOC) was determined using a 5000 TOC Shimadzu analyzer. The selectivity toward CO_2 was calculated using the following relation:[10] $SCO_2 = (X_{TOC}/X_{p\text{-cresol}}) \times 100$, where $X_{TOC} = [(TOC_o - TOC)/TOC_o] \times 100$; TOC_o = TOC value at $t = 0$ and TOC = value at different t; $X_{p\text{-cresol}}$ = conversion of *p*-cresol (%). The initial rate (in mmol h^{-1} g_{cat}^{-1}) was calculated using the TOC conversion values $r_i = (\Delta TOC(\%)/\Delta t)$ ($[polluant]_i \times m_{cat}$), were: $(\Delta TOC(\%)/\Delta t)$ = initial slop obtained from the TOC conversion as function of time curves; $[pollutant]_i$ = initial concentration of the pollutant and m_{cat} = mass of catalyst.

Table 1. Specific Surface and Mean Pore Size Diameter for Al_2O_3, ZrO_2, and $Al_2O_3-ZrO_2$ Supports

support	mean pore diameter (Å)	specific surface area (m^2 g^{-1})
Al_2O_3	122	161
$Al_2O_3-ZrO_2$1%	94	216
$Al_2O_3-ZrO_2$5%	90	215
Al_2O_3- $rO_2$10%	76	212
Al_2O_3-$rO_2$20%	76	202
ZrO_2	25	25

RESULTS AND DISCUSSION

The specific surface area (BET) and mean pore diameter of the supports are reported in Table 1 where it can be seen that addition of ZrO_2 to the alumina increases the specific area of the reference supports. For Al_2O_3 and ZrO_2 the BET areas were 161 m^2 g^{-1} and 25 m^2 g^{-1}, respectively, while for the mixed oxides the BET areas increase to 216, 215, 212, and 202 m^2 g^{-1} for 1, 5, 10, and 20 wt % of ZrO_2 content in the mixed oxide, respectively. The increase in the specific area showed by the mixed oxides can be explained by the preparation method used. The zirconium butoxide was added during preparation to peptized boehmite producing a strong modification in the hydrolysis−condensation reactions occurring in both peptized boehmite and zirconium alkoxide. Thus the textural properties of the mixed oxides were notably improved. The $Al_2O_3-ZrO_2$ mixed oxides show mean pore diameters between 94−76 Å, which are between the 122 and 25 Å showed for Al_2O_3 and ZrO_2 reference supports, respectively. On silver-containing supports any substantial modification on the specific surface areas or mean pore diameter was noted.

XRD diffractograms for Ag/Al_2O_3, Ag/ZrO_2, and $Ag/Al_2O_3-ZrO_2$ catalysts are shown in Figure 1. For alumina the X-ray diffraction pattern shows the characteristic peaks for γ-Al_2O_3 at 2θ: 30, 46, and 68. On the other hand, for ZrO_2 the X-ray diffraction pattern shows three peaks in 2θ: 30, 50.5, and 60.3 which correspond to the tetragonal crystalline structure of zirconium oxide accompanied by peaks at 2θ: 28.3 and 31.6,

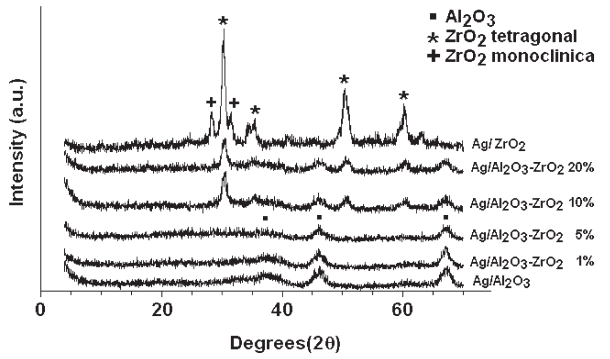

Figure 1. XRD patterns of the Ag-supported catalysts.

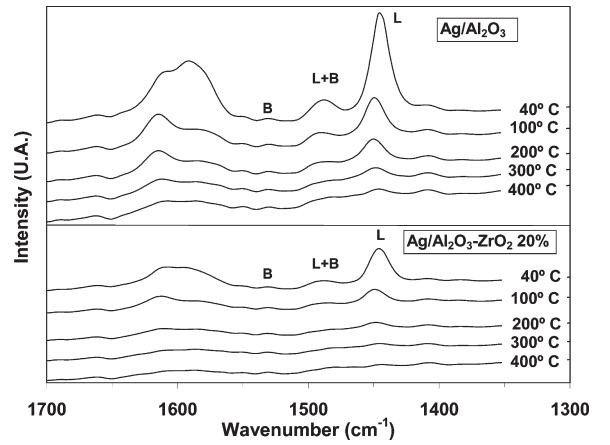

Figure 2. FTIR spectra of pyridine adsorption on Ag/Al_2O_3 and $Ag/Al_2O_3-ZrO_2$20% catalysts.

which are assigned to the zirconia monoclinic crystalline structure.[25] Then a mixture of the monoclinic and tetragonal crystalline structures where obtained in the ZrO_2 reference sample. For the catalysts containing 1 and 5% of ZrO_2 only the peaks indentifying γ-alumina can be observed, suggesting that ZrO_2 is well dispersed on the Al_2O_3 support and hence cannot be detected by XRD due to the small size of the conglomerates. For the mixed oxides at high ZrO_2 content (10 and 20 wt %), the diffractograms showed the peaks identifying γ-alumina and tetragonal ZrO_2. No peaks corresponding to zirconium oxide with monoclinic crystalline structure were detected. Thus the alumina inhibited the formation of the monoclinic form and stabilized the tetragonal structure. In the XRD patterns the peaks corresponding to silver should be placed at 2θ: 38, 44, 65, and 78; however, they cannot be seen. This can be due either to the wavelength of the peaks corresponding to metallic Ag, which appears very close to the alumina signals, where alumina is probably masking the silver peaks or to such a low concentration of Ag that it cannot be detected by this technique.[26,27]

The pyridine adsorbed FTIR spectra as a function of the temperature for two selected samples, Ag/Al_2O_3 and $Ag/Al_2O_3-ZrO_2$10% are shown in Figure 2. Pyridine adsorption has been reported as a good method to determine the properties and nature of the sites (Lewis or Brönsted) on metal oxides. The FTIR pyridine absorption spectra on Ag/Al_2O_3 shows an absorption band at 1445 cm^{-1} which has been assigned to the adsorption of pyridine coordinated on Lewis acid sites and two

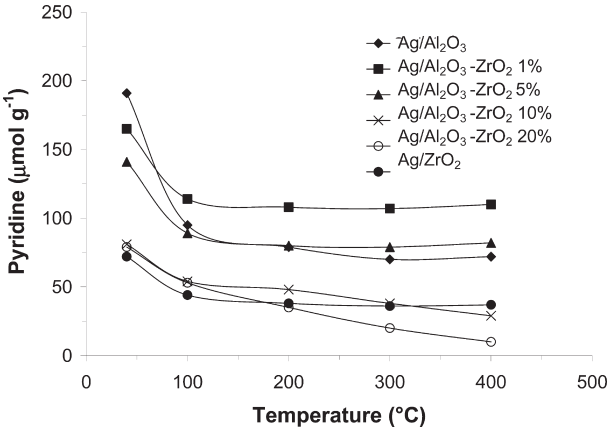

Figure 3. Pyridine adsorbed as a function of the desorption temperature for the Ag supported catalysts.

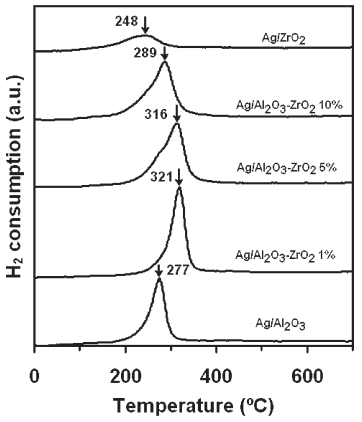

Figure 4. H_2 uptake profiles during the TPR experiments of the Ag supported catalysts.

absorption bands at 1490 and 1600 cm^{-1} associated to the presence of Lewis and Brönsted acid sites and the weak Lewis acid sites, respectively. It must be noted that the band at 1545 cm^{-1} assigned Brönsted acid sites is not present on these catalysts. In Figure 2, it can be observed that the bands intensity decreases as desorption temperature increases. The amount of adsorbed pyridine (μmol g^{-1}) for the different Ag supported catalysts as a function of the desorption temperature are shown in Figure 3. The addition of ZrO_2 to alumina on the $Ag/Al_2O_3-ZrO_2$ catalysts produces a decrease in the total acidity. It can be assumed that a modification on the acid strength and distribution occurs in the $Al_2O_3-ZrO_2$ mixed oxides. This modification could affect the adsorption properties of the Ag deposited on the surface of these mixed oxide solids.

The H_2-TPR thermograms for various solids are shown in Figure 4. It can be observed that Ag on $Al_2O_3-ZrO_2$ mixed oxides presents a higher temperature of reduction of around 289−321 °C with respect to Ag supported on Al_2O_3 (277 °C) and ZrO_2 (248 °C). The shift to higher reduction temperatures can be related to the stabilization of Ag on the larger surface area shown by the mixed oxide supports.

Infrared spectra of chemisorbed CO on Ag for two selected catalysts are shown in Figure 5 and the corresponding infrared frequencies (ν) for all the catalysts are reported in Table 3. The

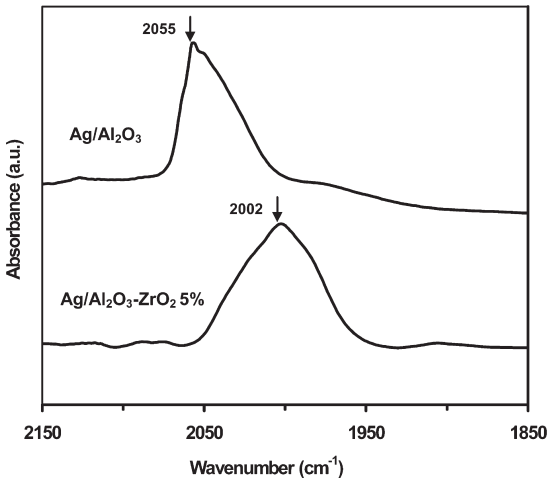

Figure 5. FTIR spectra of CO adsorbed on Ag/Al_2O_3 and $Ag/Al_2O_3-ZrO_2$5% catalysts.

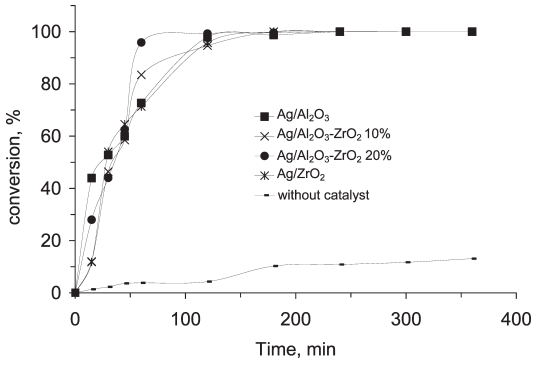

Figure 6. CWAO of *p*-cresol on Ag/catalysts (T = 160 °C; P_{O_2} = 15 bar).

Table 2. Activity and Selectivity for the Catalytic Wet-Air Oxidation of *p*-Cresol after 1 h of Reaction[a]

catalyst	r_i[b] (mmol h^{-1} g_{cat}^{-1})	abatement TOC (%)	*p*-cresol conversion (%)	selectivity to CO_2 (1 h) (%)
Ag/Al_2O_3	0.7	13	73	18
$Ag/Al_2O_3-ZrO_2$1%	2.1	21	56	37
$Ag/Al_2O_3-ZrO_2$5%	3.0	34	65	61
$Ag/Al_2O_3-ZrO_2$10%	4.9	40	77	51
$Ag/Al_2O_3-ZrO_2$20%	14.0	50	96	52
Ag/ZrO_2	1.1	9	71	12

[a] $P(O_2)$ = 15 bar, catalyst = 1 g L^{-1}, $[C_7H_8O]_i$ = 9.3 mmol L^{-1}. [b] Initial rate of TOC conversion.

Ag supported on alumina and zirconia present absorption bands at 2055 and 2031 cm^{-1} respectively, whereas, for Ag supported on $Al_2O_3-ZrO_2$ mixed oxides, the bands are shifted to lower frequencies, 2012−2002 cm^{-1}. This behavior can be attributed to differences on the Ag surface properties due to interactions with supports having different textural properties. It can be assumed that on Ag/Al_2O_3 and Ag/ZrO_2 the Ag particles have different electron density to that of silver deposited on $Al_2O_3-ZrO_2$ mixed oxides.

Table 3. Infrared Frequencies (ν, cm^{-1}) for Chemisorbed CO on Ag-Supported Catalysts

Ag/Al_2O_3	2055
$Ag/Al_2O_3-ZrO_2$5%	2002
$Ag/Al_2O_3-ZrO_2$10%	2012
$Ag/Al_2O_3-ZrO_2$20%	2010
Ag/ZrO_2	2031

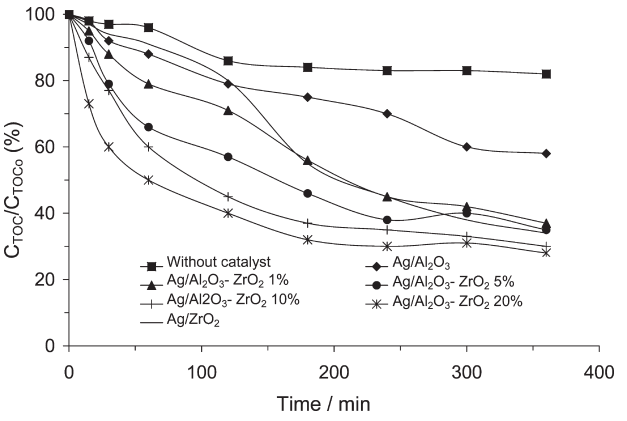

Figure 7. Normalized TOC concentration reduction (%) as a function of time for Ag-supported catalysts in *p*-cresol CWAO.

In Figure 6 the conversion of *p*-cresol as a function of time for the various catalysts is shown, where an undefined behavior can be observed. However, since the *p*-cresol degradation in absence of catalyst is practically null, the catalytic effect of the silver catalysts can clearly be seen. Total oxidation of *p*-cresol for all the catalysts is reached after 2 or 3 h of reaction (Figure 6).

To disclose the support effect in the *p*-cresol in Table 2 conversions after 1 h of reaction are reported. For Ag/Al_2O_3 and Ag/ZrO_2, catalysts conversions of 73 and 71%, respectively, were obtained, while a maximum conversion up to 96% is obtained with the $Ag/Al_2O_3-ZrO_2$20% catalyst. The *p*-cresol degradation as a function of time is a good indicator of the activity of the catalysts. However, the determination of the remaining total organic compounds in the solution containing the pollutant compound indicates the selectivity of the catalysts for the total conversion of organic compound to CO_2 and H_2O. Normalized TOC concentration reduction as a function of time for the various catalysts is shown in Figure 7. The initial rates (at t = 0) calculated from Figure 7 are reported in Table 2.

Higher initial rates were obtained with the mixed oxides when compared with Al_2O_3 or ZrO_2 reference catalysts. In Table 2 a notable high activity for catalysts containing 20 wt % of ZrO_2 can be seen. TOC abatement and selectivity to CO_2 after 1 h of reaction are also reported in Table 2. The better TOC abatement of 50% and the highest mineralization to CO_2, 61%, was obtained with the $Ag/Al_2O_3-ZrO_2$ catalysts. Figure 8 shows the percentage of mineralization to CO_2, where a maximum of selectivity to CO_2 in $Ag/Al_2O_3-ZrO_2$ catalysts can be observed.

The high activity and selectivity presented by $Ag/Al_2O_3-ZrO_2$ catalysts can be due to different metal−support interaction-inducing modifications in the electronic density of silver particles. According to the CO absorption FTIR spectra Ag surface particles on $Al_2O_3-ZrO_2$ are electron-rich, whereas on alumina and zirconia simple oxides the Ag surface particles are electron deficient. The adsorption of the reactant molecule on

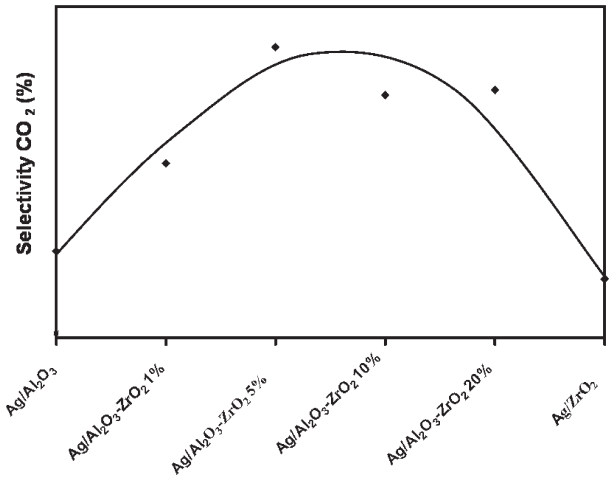

Figure 8. Selectivity to CO_2 for Ag/Al_2O_3, Ag/ZrO_2, and $Ag/Al_2O_3-ZrO_2$ catalysts in *p*-cresol CWAO.

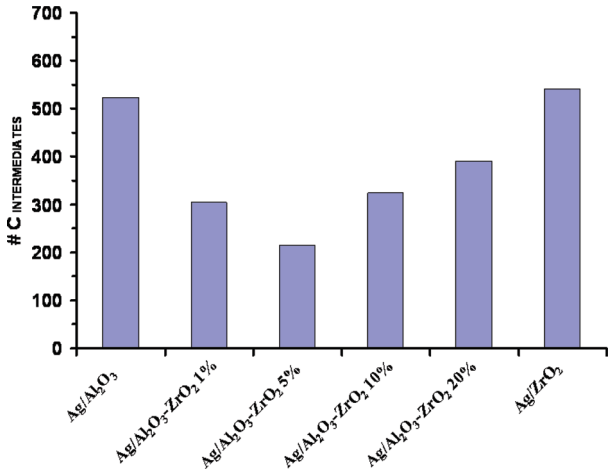

Figure 9. Number of intermediate carbons after 1 h of reaction for Ag/Al_2O_3, Ag/ZrO_2, and $Ag/Al_2O_3-ZrO_2$ catalysts in *p*-cresol CWAO.

the $Ag/Al_2O_3-ZrO_2$ surface was favored, and therefore a faster oxidation of the adsorbed species occurred and an increase in the activity and degradation of the pollutant was obtained. Since the total degradation of *p*-cresol was not attained even after 3 h of reaction, the number of the intermediates (4-methylcatechol, 4-hydroxybenzaldehyde, 4-hydroxybenzylalcohol) remaining in the polluted solution is reported in Figure 9. A low concentration of byproduct with $Ag/Al_2O_3-ZrO_2$ catalysts was found. These results are in agreement with previous data reported in the literature for different catalysts,[28] in which 4-hydroxyphenyl alcohol was obtained by oxidation of the methyl group of *p*-cresol, followed by the formation of 4-hydroxybenzaldehyde. It is also proposed that the intermediate 4-methylcatechol is obtained by oxidation at the ortho position of the aromatic ring with respect to the hydroxyl group of the *p*-cresol.[29]

CONCLUSIONS

$Al_2O_3-ZrO_2$ mixed oxides showing high specific surface areas were obtained by simultaneous peptization of boehmite and zirconium alkoxide hydrolysis. $Ag/Al_2O_3-ZrO_2$ catalysts with lower acidity than Ag/Al_2O_3 and Ag/ZrO_2 catalysts were obtained. A modification of the Ag adsorption properties were detected on the $Ag/Al_2O_3-ZrO_2$ catalysts. Improved activity for the *p*-cresol catalytic wet-air oxidation was observed with the $Ag/Al_2O_3-ZrO_2$ catalysts. Higher selectivity to CO_2 was reached in the catalyst at high zirconia content. The higher activity showed by the $Ag/Al_2O_3-ZrO_2$ catalyst is explained by the metal support interaction occurring between the mixed oxides and deposed silver.

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