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Comparative study of support effects in ruthenium catalysts applied for wet air oxidation of aromatic compounds

E. Castillejos-López [a], A. Maroto-Valiente [a], D.M. Nevskaia [a], V. Muñoz [a,b], I. Rodríguez-Ramos [b,c], A. Guerrero-Ruiz [a,b,*]

[a] Dpto. de Química Inorgánica y Técnica, UNED, Avda. Senda del rey, no. 9, 28040 Madrid, Spain
[b] Grupo de Diseño y Aplicación de Catalizadores Heterogéneos, Unidad Asociada UNED-ICP (CSIC), Spain
[c] Instituto de Catálisis y Petroleoquímica, CSIC, Campus de Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

Catalytic wet air oxidation (CWAO) reactions of aniline and phenol were conducted over supported ruthenium catalysts. Three support materials were employed: ZrO_2 and graphite, which exhibit medium adsorption capacities for pollutants and present mesopores in their texture, and an activated carbon. This latter has higher adsorption capacity for pollutants because of the large capability of the micropores for contaminant retention from water. The Ru catalysts supported on the activated carbon material showed the higher values of conversion in the oxidation of aniline and of conversion and mineralization in the reaction of phenol. Under our experimental conditions the role of micropores present on the support material seems to be relevant for improving catalytic performances. The incorporation of Ru nanoparticles from different precursors has been also evaluated. Even if the final Ru particle size is a key parameter for the catalytic mineralization, a cooperative effect with the activated carbon support has been established.

1. Introduction

Industrial plants generate increasing amounts of wastewater contaminated with toxic and hazardous organic compounds, which cause severe problems for the environment. These industrial wastewaters must be treated in order to meet the specifications for discharge or for recycling in the process [1–3]. In the latter years, the elimination techniques of organic compounds in wastewater streams have been the subject of intensive research. As one of the pollutants abatement technologies for wastewater streams that contain toxic compounds too dilute to apply incineration procedures and, also, with toxicity too high to use bio-treatments, catalytic wet air oxidation (CWAO) can provide efficiency in oxidizing highly toxic and non-biodegradable industrial effluents under relatively mild conditions (398–493 K, 5–50 bar) [4–8]. Depending on the reaction conditions and catalyst composition, either a total mineralization of pollutants into CO_2, N_2 and H_2O or an increase of the effluent biodegradability by forming easily biodegradable by-products such as carboxylic acids can be achieved [9]. Various heterogeneous catalysts have been synthesized and tested in the last decades, based either on metal oxides (Cu, Zn, Co, Fe, Mn, and Bi) or supported noble metals [7]. These catalysts have been reported to exhibit good activity for CWAO, but leaching of the active ingredients has been detected, making them unattractive [7]. Furthermore, the majority of metallic (Pt, Pd, Ru) supported catalysts developed for CWAO show serious deactivation problems, including poisoning and fouling, in addition to leaching. Moreover, the support material may suffer from stability problems, such as dissolution in the reaction medium or poor chemical resistance [10]. As a result, researchers are looking for more stable and active heterogeneous catalysts.

Among the possible pollutants, nitrogen containing aromatic and phenolic compounds, which come from dye and textile industry, represents more than 20% of them. In addition, while oxidizing nitrogen containing aromatic compounds, phenol appears as a key component [9]. These two group compounds have very high toxicity and therefore their elimination is required. This paper is focused on CWAO of aniline and phenol. In addition, among noble metals ruthenium is very active for the conversion of a wide range of organic compounds and selective into carbon dioxide [9].

The aim of this work is to investigate the behaviour of various supported ruthenium catalysts in the CWAO reaction of aniline

* Corresponding author at: Dpto. de Química Inorgánica y Técnica, UNED, Avda. Senda del rey, no. 2, 28040 Madrid, Spain. Tel.: +34 915 854765.
E-mail address: aguerrero@ccia.uned.es (A. Guerrero-Ruiz).

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and phenol. Three types of supports and ruthenium precursors were employed to generate the supported metal clusters. The catalysts were characterized by the combination of several techniques in order to correlate the catalyst behaviour with its surface properties.

2. Experimental

2.1. Catalysts

The supports used in the preparation of the ruthenium catalysts are: (1) ZrO_2 prepared from zirconium hydroxide stabilized with 3.5% SiO_2 (MEL, zirconium hydroxide) calcined at 973 K, (2) HSAG (mesoporous high surface area graphite from Lonza), previously treated in N_2 flow at 1173 K to remove surface groups, and (3) AC (commercial activated carbon provided by ICASA company, Cordoba, Spain). AC was previously purified by treatment with HCl and HF solutions to remove inorganic compounds and subsequently treated on N_2 flow at 1173 K. The ruthenium catalysts (2 wt% metal loading) were prepared by impregnation of the supports with an excess of solvent volume in a rotator-evaporator with solutions of the precursors. After drying the samples in air at 373 K, the resulting solid was reduced at 623 K for 2 h in hydrogen flow. Nomenclature of the different supported Ru catalysts and a summary of the conditions used for their preparation (ruthenium precursor salt, solvent/s and supports) are listed in Table 1.

2.2. Characterizations

Temperature-programmed reduction (TPR) measurements were carried out in a quartz microreactor with 200–300 mg of prepared sample, under a continuous flow of 20 mL min^{-1} of a H_2/He gas mixture (10% H_2). The temperature was increased from room temperature to 800 K at 2 K min^{-1}. H_2 consumption, as well as decomposition products (NO, CO, CO_2 and CH_4), was measured by on-line gas chromatography (Varian 3400) using a thermal conductivity detector (TCD).

The determination of the specific surface area (S_{BET}) of the supports and the catalytic materials was carried out by physical adsorption of N_2 at 77 K in a Micromeritics ASAP 2010 apparatus. The metallic dispersions and particle size were determined from the CO and H_2 chemisorption isotherms. Prior to the chemisorption measurements, catalyst samples were reduced "in situ" at 673 K for 2 h under hydrogen and outgassed at the same temperature for 1 h. Hydrogen and carbon monoxide chemisorption isotherms were determined in a glass-vacuum system with a capacitance manometer MKS for pressure measurements. Extrapolation of the hydrogen isotherm to zero pressure and the two isotherms method for carbon monoxide were applied in order to determine the uptake of these gases. The number of exposed metal atoms was calculated assuming an atomic stoichiometry of Ru/H = 1/1 and Ru/CO = 1/1 [11].

Table 1
Nomenclature and main preparation conditions of the supported ruthenium catalysts.

Catalyst	Precursor: solvent	Support
RuCOZr	$Ru_3(CO)_{12}$: tetrahydrofurane	ZrO_2
RuAcZr	$Ru(C_5O_2H_7)_3$: ethanol	ZrO_2
RuClZr	$RuCl_3{\cdot}xH_2O$: ethanol	ZrO_2
RuCOG	$Ru_3(CO)_{12}$: tetrahydrofurane	HSAG
RuAcG	$Ru(C_5O_2H_7)_3$: ethanol	HSAG
RuClG	$RuCl_3{\cdot}xH_2O$: ethanol	HSAG
RuCOC	$Ru_3(CO)_{12}$: tetrahydrofurane	AC
RuAcC	$Ru(C_5O_2H_7)_3$: ethanol	AC
RuClC	$RuCl_3{\cdot}xH_2O$: ethanol	AC

2.3. Oxidation reactions

CWAO experiments were performed in a stainless-steel high pressure autoclave (Parr Instruments Co., USA, 5521) with a volume of 300 mL, capable of running batch experiments at pressures up to 2 MPa and temperatures up to 623 K. The reactor is equipped with a stirrer, regulated electronically, with rotation speed of 500 rpm being chosen to ensure proper mass transfer of air in the liquid phase. A constant temperature was maintained with an electronic controller. A 0.16 L aliquot of an aqueous solution containing approximately 20–23 mmol L^{-1} of reactant (aniline or phenol) and 4 g l^{-1} of the pre-reduced catalyst was fed into the reaction vessel. The solution was first purged with helium to remove any traces of oxygen and then heated to 413 K. This procedure was used to minimize the unwanted reactant conversion during the heating-up period. As soon as the set temperature was achieved, the reactor was filled with pure oxygen and the oxygen partial pressure was maintained at 20 bar. The reactants were pure grade Fluka (>99%).

The liquid phase was analyzed by HPLC on a Hypersil C18 column using a mixture of an aqueous solution of 0.03 M K_2HPO_4 and acetonitrile as the gradient mobile phase. Flow rate of the mobile phase was 1 mL min^{-1} and detection was through a UV detector set at 254 nm wavelength. The gas phase was analyzed on a GC equipped with a Porapak Q packed column (1/8 in., 2 m). Concentration in the gas phase was determined by standardization with the O_2 peak as reference while the carbon dioxide dissolved in water was calculated from calibration curve giving the concentration of CO_2 in water versus its partial pressure in gas phase. These analyses allowed calculation of the percentages of conversion and mineralization (i.e. the percentage of reactant oxidized into CO_2) as well as de initial rates in mmol h^{-1} $g_{Ru}{}^{-1}$. The initial concentration used in the calculation of the transformation rate was the concentration measured just before the introduction of O_2 in the reactor, that is, after heating period. It was a way to account for the thermal reaction and the adsorption of the reactant that could make us overestimate the catalyst activity for oxidation.

On the other hand, at the end of CWAO test, the catalysts used were carefully collected and dried at 343 K to remove the excess water. Thermal gravimetric analysis (TGA) of these samples was carried out using a $SDTQ_{600}$ 5200 TA System. Samples of about 40 mg were treated at room temperature for 30 min under nitrogen (flow rate =100 mL min^{-1}). Then, the system was heated to 1273 K, with a heating rate of 10 K min^{-1}.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the TPR profiles of the different supported Ru catalysts. RuAcZr exhibits a well-defined hydrogen consumption peak at 539 K with a shoulder at 480 K. In this case, both peaks appear along with CH_4, CO and CO_2 evolution. Therefore, both peaks would correspond to decomposition and reduction of the precursor acetylacetonate ligands to CO, CO_2 and CH_4, and simultaneous metal reduction from Ru(III) to Ru^0 species. On TPR profiles of RuAcG and RuAcC, appear a broad peak in this range of temperatures (450–573 K), which probably includes also these two processes (decomposition and reduction). As for catalysts prepared from ruthenium chloride, RuClG and RuClC show a broad hydrogen consumption at the 450–573 K range, with maxima at

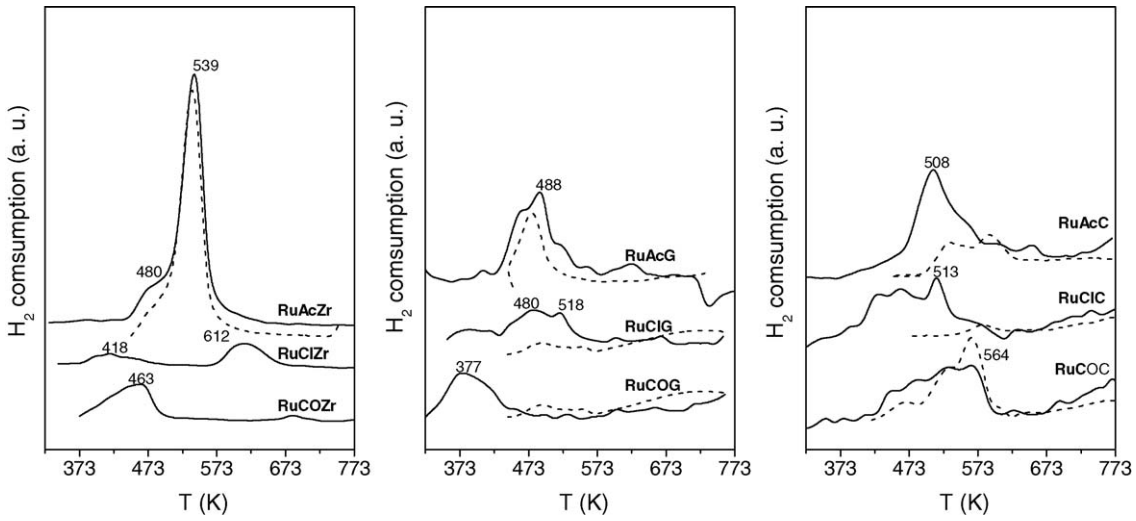

Fig. 1. TPR profiles for H_2 of the ruthenium catalysts. Full lines: total H_2 consumption; dotted lines: CH_4 formation.

480 and 518 K, and 513 K respectively, while RuClZr shows two peaks at 418 (small) and at 612 K. This latter peak, clearly centred at a temperature higher than for other two catalysts, is probably due to the presence of Ru centres with SMSI (support-metal strong interaction). The TPR profiles of the catalysts prepared with $Ru_3(CO)_{12}$ show hydrogen consumption at 373–473 K corresponding to the reduction of CO evolved in the carbonyl decomposition. The hydrogen consumption at higher temperatures (564 K) in the RuCOC profile is attributed to the support gasification.

BET surface area of the catalysts and the ruthenium dispersions determined both from hydrogen and carbon monoxide chemisorptions are given in Table 2. The impregnation of the support with the ruthenium salt only has remarkable consequences on S_{BET} of graphite-supported catalysts. In this sense, RuClG sample has the lowest value of S_{BET} among the graphite-supported catalysts. When comparing the CO and hydrogen chemisorption data in Table 2, it is seen that the H/CO ratio, for all the cases with the exception of the RuCl/AC sample, is higher or lower than one. This lack of coincidence between hydrogen and carbon monoxide obtained dispersions could be due to changes in the assumed Ru:CO = 1:1 stoichiometry for the CO chemisorption. Although the stoichiometry Ru:CO = 1:1 is accepted in a general way, formation of bridged (Ru:CO = 2:1) and subcarbonyl (Ru:CO = 1:2) species has also been described [12,13]. In addition an increase of the Ru:H = 1:1 stoichiometry due to activation phenomena has been reported for catalysts containing chloride or acid species [14,15] where inhibition of the hydrogen adsorption was found. Therefore, this latter may be the case for RuClZr and RuClC catalysts. In general, Table 2 shows that there is not coincidence between the ruthenium dispersion values obtained from adsorption of hydrogen and those obtained from adsorption of CO. In spite of these discrepancies, in general it can be said that the ruthenium catalysts supported on the activated carbon have the lower dispersions independently of the metal precursor employed. It seems that the use of a microporous support as activated carbon make more difficult the dispersion of the active phase. However on the zirconia support and with the carbonyl precursor the ruthenium is monoatomically dispersed.

Table 2
Main surface properties of ruthenium catalysts.

Sample	S_{BET}	H/Ru	CO/Ru	H/CO
ZrO_2	101	–	–	–
RuCOZr	88	1.1	1.30	0.8
RuAcZr	102	0.32	0.07	4.6
RuClZr	78	0.09	0.25	0.4
HSAG	193	–	–	–
RuCOG	163	0.59	0.39	1.5
RuAcG	130	0.07	0.08	0.9
RuClG	122	0.10	0.21	0.5
AC	986	–	–	–
RuCOC	1091	0.14	0.15	0.9
RuAcC	986	0.04	0.03	1.3
RuClC	986	0.14	0.13	1.1

3.2. Reaction mechanism and temperature effect

A series of blank experiments (WAO without catalyst) were carried out at 2 MPa of O_2 and at two different temperatures (413 and 473 K). Fig. 2 shows the variation of the by-products concentration, conversion, and mineralization values versus reaction time obtained from these experiments. According to the mechanisms proposed for the phenol and aniline oxidation [9,16–22] the reaction can follow the reaction pathways summarized in Fig. 3. The WAO of aniline is known to lead to the formation of some azo compounds (hydrazobenzene, azobenzene and azoxybenzene), nitrogenous aromatic compounds (p-aminophenol, nitrobenzene, p-nitrophenol and nitrosobenzene) and other aromatics (phenol, hydroquinone, catechol and benzoquinone) [18]. WAO oxidation of phenol yields products of complete oxidation (carbon dioxide and water) and products of partial oxidation (quinones, diols, a mixture of carboxylic acids including maleic acid) [18,19].

Fig. 2 shows that at 473 K only nitrobenzene was detected as intermediate product of the aniline oxidation. This fact reveals that aniline is oxidized by the formation of this intermediate but the aniline oxidation through the aminophenol formation can not be discarded (Fig. 3), because by-products of the two oxidation routes present different reactivity towards oxidation. Thus, it has been reported a decreasing order of reactivity of aminophenol > nitrophenol > nitrobenzene for the CWAO at 473 K on Ru/CeO_2 catalysts [20]. On the other hand, the phenol oxidation at 473 K goes through the formation of hydroquinone and p-benzoquinone as the by-products (Fig. 2). Probably, this is a consequence of the reaction conditions, O_2 excess or near stoichiometric conditions, employed in this work [22].

As it can be expected (Fig. 2), the phenol and aniline conversion and mineralization increase with the increasing temperature.

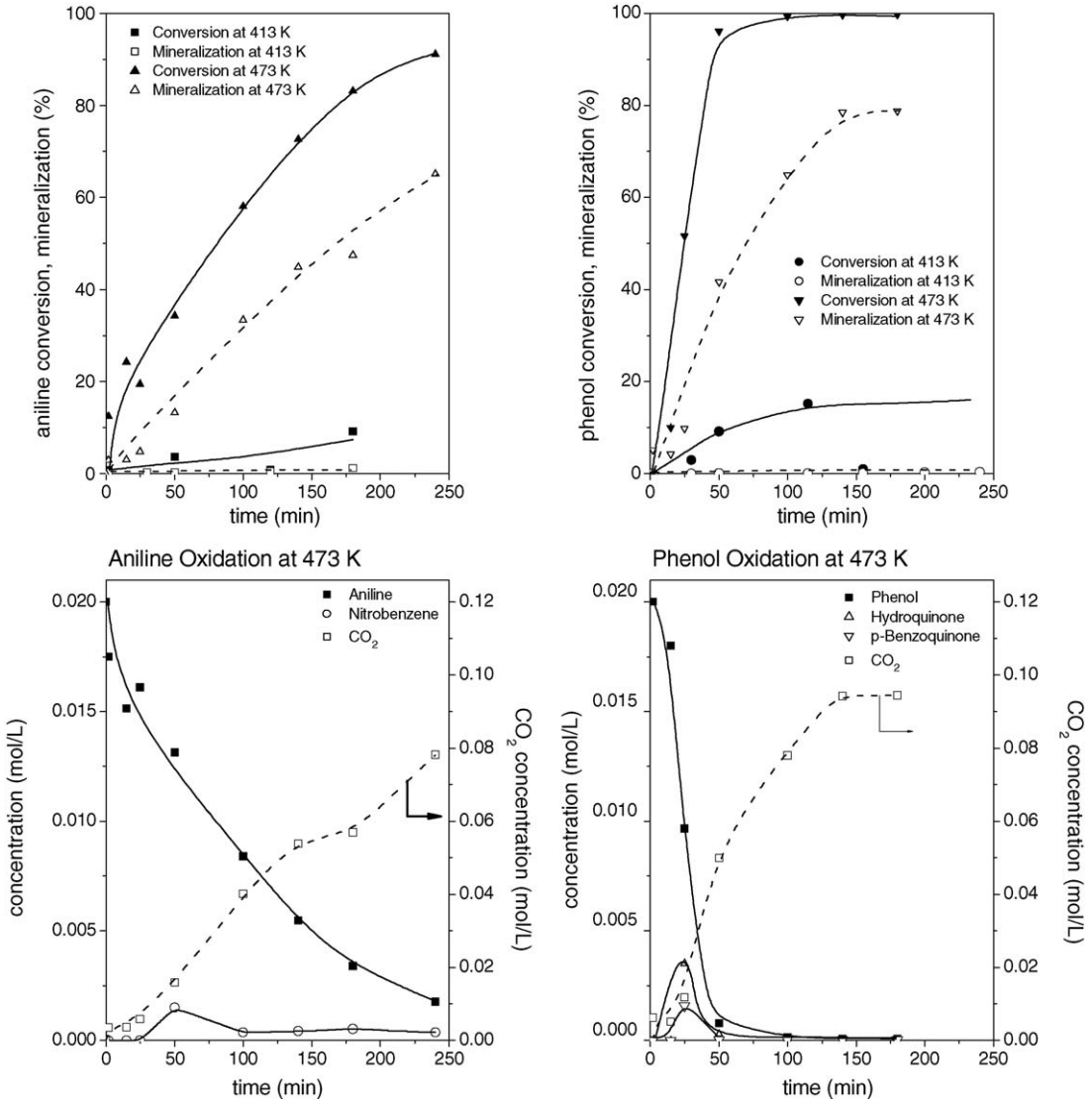

Fig. 2. Aniline and phenol oxidation without catalyst.

Without catalyst a temperature of 473 K is necessary to obtain significant conversions and mineralization. Thus, the conversion of aniline and phenol reaches a 10% and 15%, respectively, at 413 K. While, at 473 K conversions of around 90% for aniline and 100% for phenol were achieved. The same trend is observed for the mineralization. These results indicate that phenol is easier oxidized into CO_2 than aniline. From the realized experiments, a reaction temperature of 413 K was chosen for the catalytic oxidation. At this temperature, nitrobenzene and p-benzoquinone were detected in some cases as intermediates in the catalytic oxidation of aniline and phenol, respectively.

3.3. Catalyst activity

Data for initial rates, calculated from conversion versus time profiles, and turnover frequencies (TOF) on catalytic wet oxidation of aniline and phenol at 413 K for supports and Ru catalysts are summarized in Table 3. The bare supports show very low initial rates (mmol h^{-1}) on CWAO of aniline and phenol, and generally these are lower than those observed on the supported ruthenium catalysts with the exception of zirconia support which presents an initial activity for CWAO of aniline with the same order of magnitude of those of the zirconia supported ruthenium catalysts. This fact suggests that the surface base/acid functionalities of the zirconium oxide have activity for the oxidation of aniline. But in terms of mineralization this support showed not significant activity (M of 0.5 or 2% after 1 or 3 h of reaction). This behaviour of zirconium oxide was already observed during oxidation of p-hydroxybenzoic acids [23]. Therefore, a clear beneficial effect of the addition of a supported ruthenium catalyst is demonstrated in Table 3.

The TOF values for aniline and phenol oxidation on ruthenium catalysts depend on both the ruthenium precursors and the supports employed for dispersion of the active phase. In general, for the same precursor, the use of activated carbon supposes a significant increment of the TOF values (between three and ten times). This higher initial activity of the activated carbon supported catalysts can be related to the high adsorption capacity of the support which is directly associated with its high surface area. Note that at time zero (corresponding to the admission of O_2 in the reactor), initial conversions using samples (bare supports and ruthenium catalysts) were not zero, because concentrations of phenol or aniline were different from the concentration introduced. This difference was due to adsorption on the solids. The

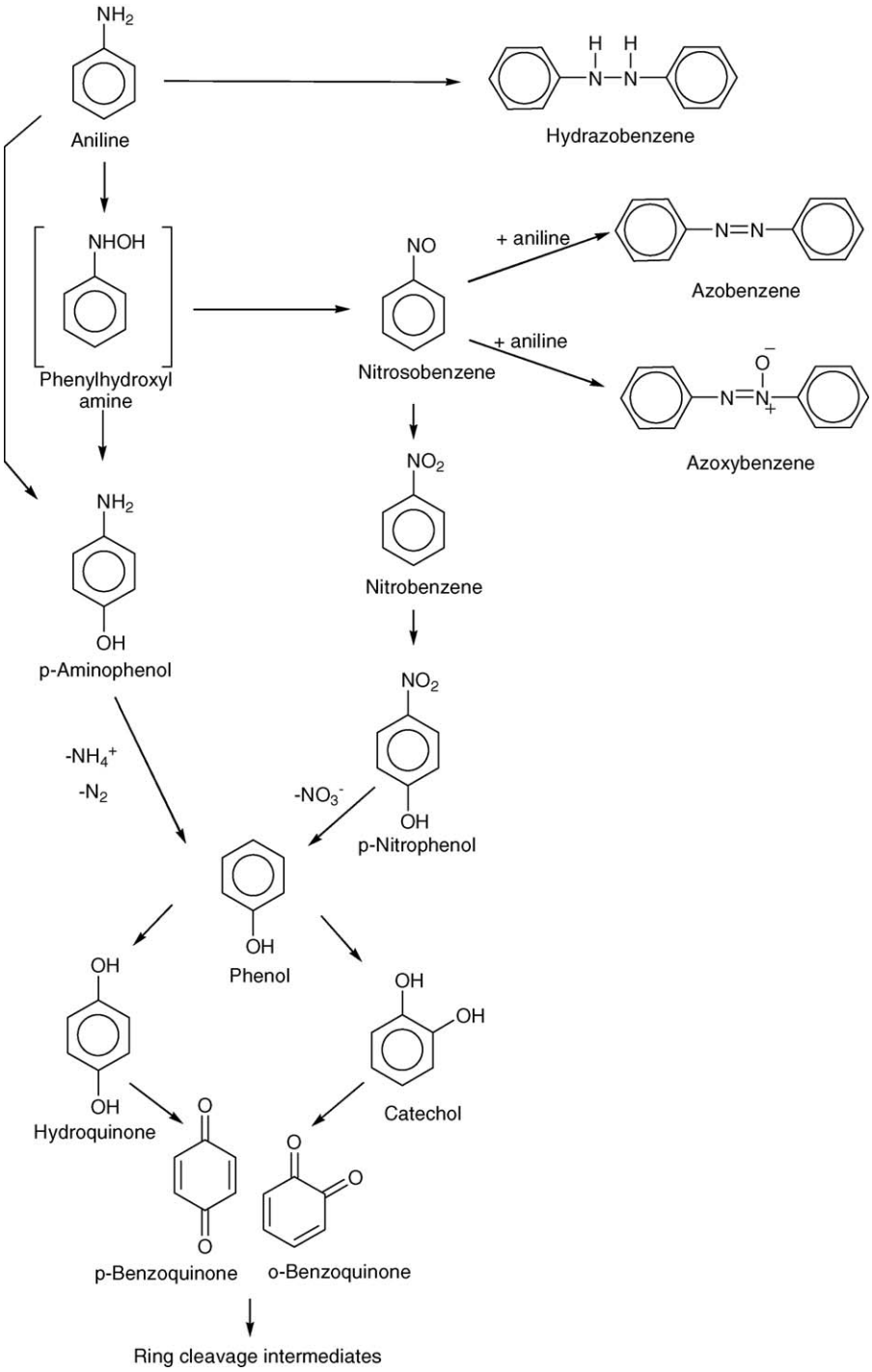

Fig. 3. Reaction scheme for the oxidation of aniline and phenol.

amounts of aniline and phenol adsorbed on the catalysts at 413 K (before O_2 admission) are reported in Table 4. Adsorption of both phenol and aniline is observed on the three supports but with different extent. A preferential adsorption of phenol on catalysts supported over activated carbon is observed, while aniline is adsorbed on the two series supported over carbonaceous materials in a higher degree. The differences in adsorption on the distinct supports are due first to the differences in surface area and second to the chemical properties of the support.

Furthermore, an effect of the ruthenium particle dispersion on the catalytic activity is seen in Table 3. Thus, samples with metallic particle size <5 nm (metal dispersion $>25\%$) show the lowest TOF values on CWAO of aniline and phenol. This behaviour is similar to that detected on these types of catalysts in previous works [17,24]. This fact has been attributed to a deactivation caused by an over-oxidation of the catalyst surface particularly noticeable in the case of very small Ru-clusters (1 nm) [24]. These activity values (TOF and initial rates; Table 3) are comparable to those obtained on previous works [9,16]. It is remarkable that the activity values for phenol oxidation on this work are higher than those observed on previous works [9,16].

Table 3
Aniline and phenol oxidation at 413 K: initial rate, turnover frequency (TOF), conversion (C) and mineralization (M).

Catalyst	Initial rate		TOF_H	Mass balance			
				After 1 h		After 3 h	
	mmol h^{-1}	mmol h^{-1} g_{Ru}^{-1}	(h^{-1})	C (%)	M (%)	C (%)	M (%)
Aniline oxidation							
ZrO_2	0.7	–	–	22	0.5	41	1
RuCOZr	0.5	39	4	10	4	30	7
RuAcZr	0.6	47	15	19	2	30	4
RuClZr	0.2	16	17	14	5	24	8
HSAG	0.1	–	–	2	0	4	0
RuCOG	0.2	19	3	10	3	29	5
RuAcG	0.4	31	44	18	2	29	4
RuClG	0.2	15	17	8	6	26	9
AC	0.4	–	–	15	2	37	1
RuCOC	0.7	59	42	25	7	45	13
RuAcC	1.4	108	269	43	8	69	13
RuClC	2.3	177	126	66	10	78	17
Phenol oxidation							
ZrO_2	0.1	–	–	1	0	1	0
RuCOZr	18.0	1385	126	56	10	81	21
RuAcZr	6.1	469	151	48	7	59	16
RuClZr	4.7	362	402	53	7	71	17
HSAG	0.1	–	–	9	1	14	2
RuCOG	3.2	250	42	70	11	95	31
RuAcG	2.4	188	268	43	4	74	14
RuClG	3.8	292	324	79	21	97	64
AC	0.1	–	–	4	1	10	4
RuCOC	7.6	585	418	74	16	94	43
RuAcC	6.3	485	1212	83	13	96	35
RuClC	22.4	1724	1232	96	24	100	70

3.4. Conversion and mineralization

Evolution of the aniline and phenol conversion with time of reaction is reported in Fig. 4 for the Ru catalysts and for the supports. Moreover, aniline and phenol conversion (C) and mineralization (M) values, after 1 and 3 h of reaction, are reported in Table 3.

3.4.1. Aniline oxidation

The catalysts supported on ZrO_2 present values of aniline conversion which are comparable to those obtained with the bare support. But the mineralization obtained with the zirconia support is very low, while this is significantly enhanced by the addition of ruthenium. Therefore the metallic function is more efficient for the oxidation of the intermediate compounds to produce CO_2 than the

Table 4
Amounts of reactant adsorbed on the catalysts at 413 K (aniline = A; phenol = P).

Catalyst	ZrO_2		RuCOZr		RuAcZr		RuClZr	
Reactant	A	P	A	P	A	P	A	P
Initial concentration (mmol L^{-1})	22.6	20.6	22.5	20.2	22.4	20.4	22.7	20.1
Concentration at 413 K before O_2 admission (mmol L^{-1})	22.3	20.55	22.3	20.15	22.3	20.35	22.6	20.05
Adsorbed amount								
mmol g_{cat}^{-1}	0.13	0.01	0.05	0.01	0.02	0.01	0.02	0.01
μmol m^{-2}	0.74	0.12	0.56	0.14	0.24	0.12	0.32	0.16
	HSAG		RuCOG		RuAcG		RuClG	
	A	P	A	P	A	P	A	P
Initial concentration (mmol L^{-1})	23.2	20.2	23.8	20.4	22.4	20.5	22.6	20.2
Concentration at 413 K before O_2 admission (mmol L^{-1})	21.7	20.1	22.8	20.2	21.4	20.4	22	20
Adsorbed amount								
mmol g_{cat}^{-1}	0.37	0.02	0.25	0.05	0.25	0.03	0.15	0.05
μmol m^{-2}	1.91	0.13	1.53	0.31	1.89	0.19	1.21	0.40
	AC		RuCOC		RuAcC		RuClC	
	A	P	A	P	A	P	A	P
Initial concentration (mmol L^{-1})	23.2	20.9	22.3	20.7	22.4	20.4	23.4	20.4
Concentration at 413 K before O_2 admission (mmol L^{-1})	16.9	14.6	16.4	13	16.9	12.6	17.9	12.7
Adsorbed amount								
mmol g_{cat}^{-1}	1.57	1.55	1.59	1.9	1.35	2.17	1.35	1.9
μmol m^{-2}	1.59	1.57	1.45	1.74	1.37	1.95	1.37	1.92

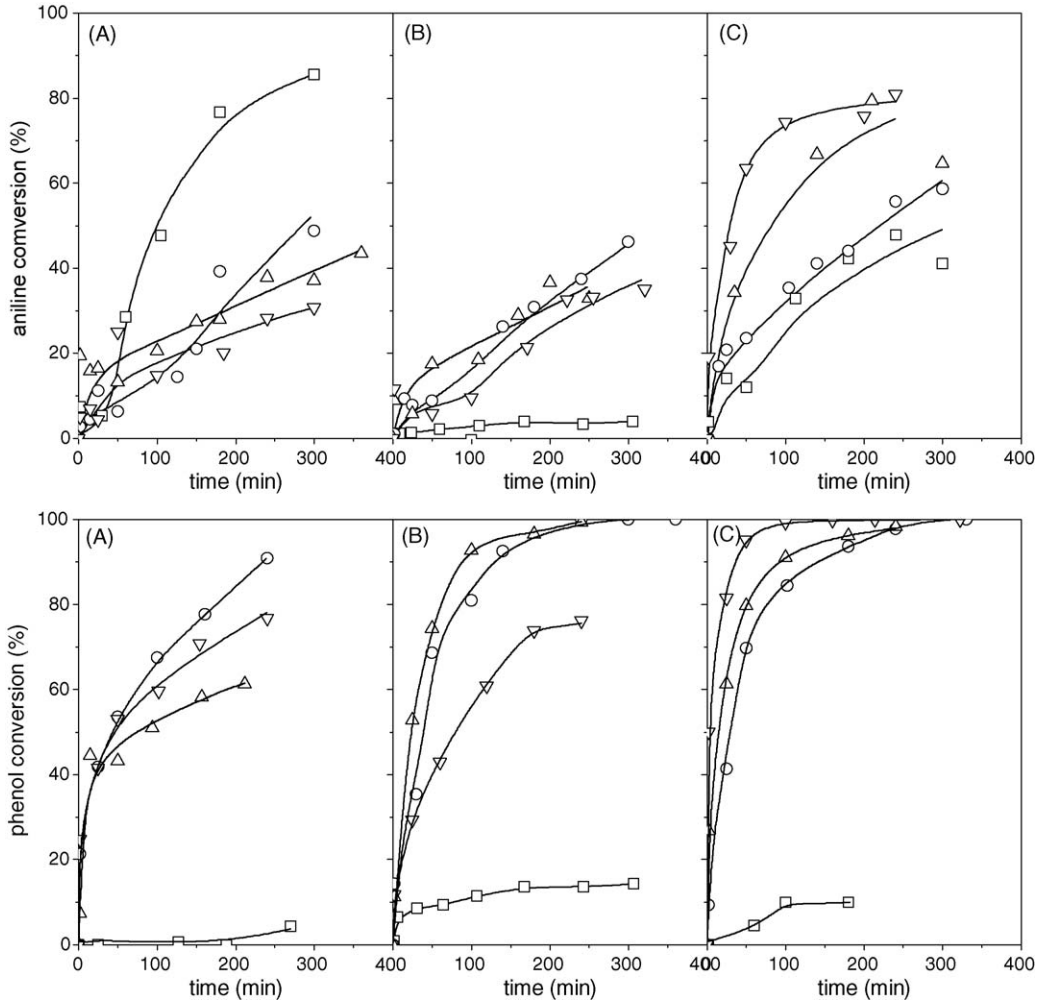

Fig. 4. Aniline and phenol conversion in CWAO on ZrO_2 (A), HSAG (B) and AC (C) supported catalysts. (□) bare support and (○) RuCOX, (△) RuAcX, and (▽) RuClX catalysts (X = ZrO_2, HSAG and AC).

zirconium oxide. In contrast, AC and HSAG supports show lower conversion values than their respective catalysts. The activated carbon supported ruthenium catalysts are the most active for the CWAO reaction of aniline. After 3 h of reaction, Ru/AC samples show conversion values approximately of 45–78% higher than those obtained on HSAG and ZrO_2 supported catalysts, which reach values approximately of 26–30%. Concerning the mineralization, the higher values are obtained on Ru/AC catalysts (Table 3). These maxima M values can be ascribed either to the lower metal dispersion of Ru/AC samples or to a cooperative effect with the micropores of AC support.

3.4.2. Phenol oxidation

The conversion values observed after 1 and 3 h reaction of CWAO of phenol on the three bare supports are much lower than those obtained with ruthenium catalysts (Table 3). Approximately 10–14% of this aromatic compound is converted after 3 h over the carbonaceous supports (HSAG and AC), which is one order of magnitude higher than the conversion observed on ZrO_2. Furthermore, catalysts supported on carbon materials (Ru/G and Ru/AC catalysts) are clearly the most active for the phenol oxidation, conversions around 95–100 are obtained after 3 h of reactions. However, although very high conversions can be obtained with carbon-supported catalysts, a total mineralization is never observed. In general, the carbon-supported catalysts give place to higher phenol conversion and mineralization values. But in relation to selectivity to CO_2, only the use of ruthenium chloride as precursor of the metallic Ru dispersed over graphite and AC supports supposes a noticeable improvement, with values close to 70%. Masende et al. [25,26] found for catalyzed oxidation reactions that the grade of surface oxidation of the metal particle influences the reaction pathways and the selectivity to CO_2. They report a diminished phenol conversion in the presence of oxygen excess, mainly caused by the catalysts deactivation as a result of the over-oxidation of the metal particle. Another consequence of these oxidative conditions was the decrease in the CO_2 selectivity and the increased production of polymeric products [26]. On the other hand, it has been reported that the presence of residual chlorine on the carbon catalyst could favour electronic interactions between Cl and the metal particles or adsorbed species [15,27]. More concretely, an electron-withdrawal induced by the chlorine anions on the metal surface is proposed [15]. This fact would provoke a drastic suppression of the oxygen adsorption capacity of the metal, preventing the over-oxidation of the ruthenium particles and giving place to a major selectivity towards the formation of CO_2 (Table 3). This behaviour also can explain the by-products distribution obtained on the AC supported catalysts, where p-benzoquinone was produced on RuCOC and RuAcC but not on RuClC.

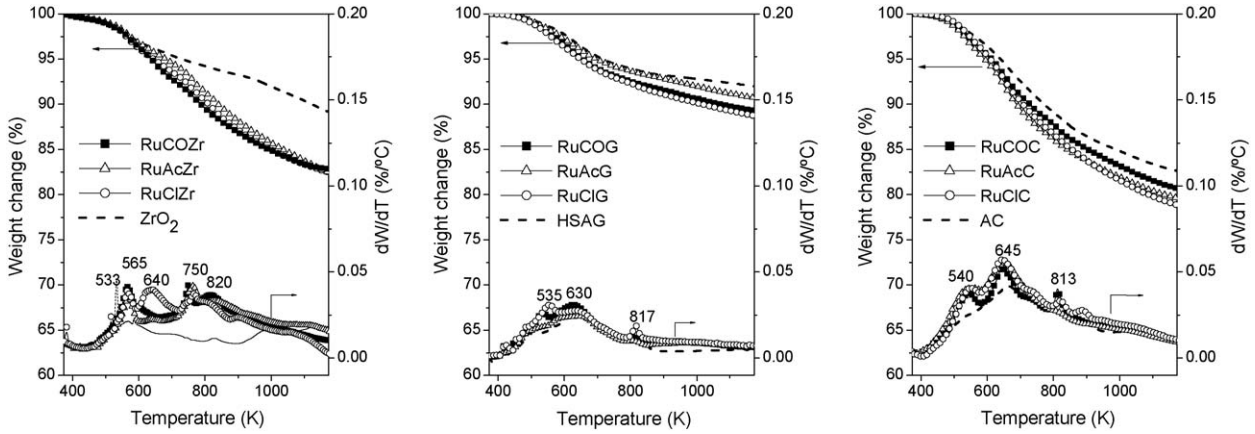

Fig. 5. TGA data and first derivative of TGA data of used catalysts alter being tested in CWAO of aniline experiments.

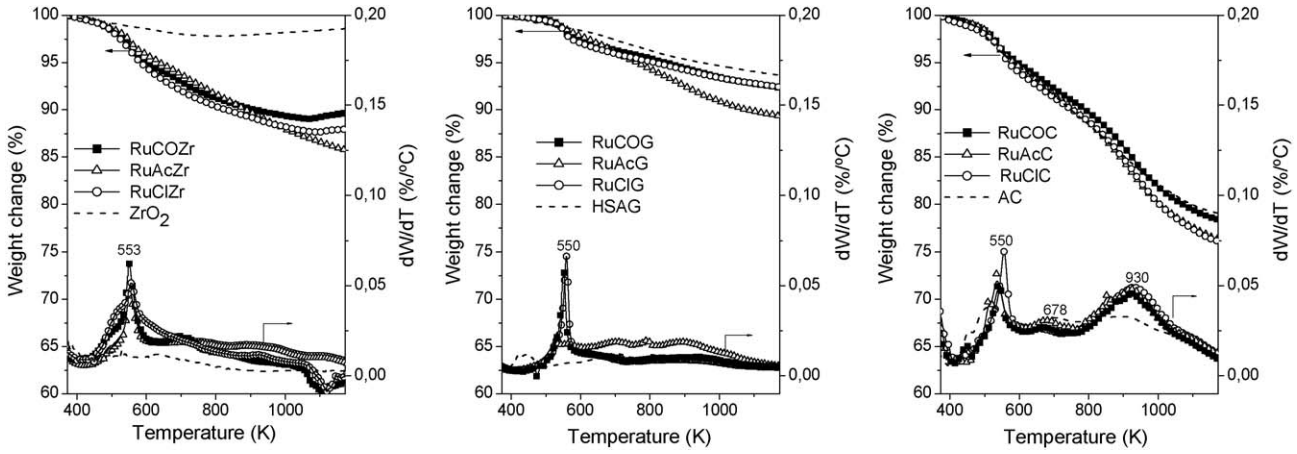

Fig. 6. TGA data and first derivative of TGA data of used catalysts alter being tested in CWAO of phenol experiments.

3.4.3. TG analysis after reaction

TGA were performed between 373 and 1173 K under nitrogen flow to evaluate the quantity and the kind of products adsorbed over the used catalysts. Figs. 5 and 6 show the thermograms and their first derivatives (dW/dT) for the used supports and catalysts. Also, total weight loss (TWL) of each sample is summarized in Table 5 for aniline and phenol CWAO reactions. Ruthenium catalysts supported on ZrO_2 show the largest differences in TWL values with respect to the bare support for both reactions. Besides, it is noticeable that Ru/AC catalysts and AC support used in the CWAO show the highest values of TWL.

Table 5
Total weight loss during the TGA of the used catalysts (%, w/w).

Catalyst	Aniline oxidation	Phenol oxidation
ZrO_2	11	2
RuCOZr	17	10
RuAcZr	18	12
RuClZr	17	14
HSAG	8	6
RuCOG	11	8
RuAcG	9	11
RuClG	11	8
AC	17	21
RuCOC	19	22
RuAcC	20	24
RuClC	21	24

Generally speaking, the DTG plots (dW/dT vs. temperature) have two zones (Figs. 5 and 6). In the first one, between 400 and 500 K, the species are slowly released; in the second one, between 600 and 1073 K, in which they are released in a continuous and rapid mode. This latter zone shows various peaks which depend on the compound used in the CWAO. Two or three peaks can be observed on samples used for CWAO of aniline, while among catalysts previously employed for phenol oxidation only one clear peak can be observed in the DTG plots of AC supported catalysts.

Both CWAO reactions can produce not identified products, possibly polymers [20,26], which are not desorbed from the catalyst surface under the reaction conditions. It is believed that the weight loss in the first zone coincides with the release of physisorbed model compounds and reaction intermediates, whereas, the weight loss in the second zone corresponds to the decomposition of chemisorbed species, including the cracking of polymers from oxidative coupling reactions [28]. In the phenol oxidation reaction, it seems that these latter species (polymers) are produced in a larger degree on catalysts supported on AC, while on graphite and ZrO_2 catalysts the phenol oxidation induces the formation of these species in minor quantity. In contrast, the formation of polymeric products during the CWAO of aniline is observed for the catalysts supported on the three supports.

4. Conclusions

Ruthenium catalysts have been supported on zirconia, graphite and activated carbon supports. Several CWAO reaction tests were performed with phenol and aniline as model compounds. The oxidation was conducted in mild conditions of O_2 pressure (2 MPa) and temperature (413 K). After 3 h of reaction, a maximum of 78% aniline conversion and a 17% of mineralization was obtained. On the other hand, for phenol reaction conversions of 100% were reached, with a 70% of mineralization as a maximum.

For the same ruthenium precursor, the use of activated carbon as support, enhance the values of conversion and mineralization. The use of $RuCl_3$ as ruthenium precursor increases the catalytic activity and the selectivity towards CO_2 formation probably because the residual chorine ions prevent the over oxidation of the ruthenium particle.

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