

Catalytic wet air oxidation of phenol aqueous solutions by 1% Ru/CeO₂–Al₂O₃ catalysts prepared by different methods

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Abstract

The wet air oxidation of phenol aqueous solutions (5 g/L) has been studied in a trickle bed reactor (140 °C and 7 atm of oxygen pressure). The experiments were performed over several 1%Ru/5%CeO₂–Al₂O₃ samples, prepared by different methods: impregnation, co-impregnation, co-precipitation and surfactant. Phenol conversion and chemical oxygen demand were evaluated. Results indicate that performance of the catalysts is influenced by the preparation method. Phenol conversions diminished with reaction time; deactivation was attributed to the deposition of carbonaceous solids on the surface and to the transformation of the support into boehmite phase. The selectivity toward CO₂ production was, in all cases, nearly complete.
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1. Introduction

Phenol and its derivatives are hazardous compounds present in the effluent streams of diverse industries. However, due to their bactericidal effect, it is not possible to treat highly concentrated phenolic wastewater using conventional (biological) sewage processing methods [1]. The Catalytic Wet Air Oxidation (CWAO) process offers an economical and technologically viable alternative for abating or reducing the toxicity of moderately concentrated, toxic, non-biodegradable organic compounds. The critical step in the implementation of this technique is the preparation of an efficient and durable catalyst.

Phenol has been studied as a model compound in many CWAO investigations [2–6]. The literature survey shows considerable variability in activity and stability among the catalysts used in this reaction, most often metal oxides

or supported noble metals [7]. Usually it is observed that catalysts formed by base-metal oxides exhibit major stability problems during reaction [6,8–11]. The deactivation process was mainly assigned to the leaching of the active phase (or support) and also to the blockage of the catalyst surface by carbonaceous products.

Different authors [12–19] reported that materials based on noble metals deposited on stable supports are active and more resistant to acid leaching than transition metal oxides. Among stable supports, ceria appears as a good alternative in terms of activity and stability [19–22].

Our purpose is to study the performance of noble metal catalysts (with a CeO₂/Al₂O₃ support) as an efficient, stable and selective alternative for the aqueous oxidation of organics. We report here the catalytic oxidation of phenol aqueous solutions in a Trickle Bed Reactor (TBR), using 1%Ru/5%CeO₂–Al₂O₃ catalysts prepared by different methods. The experiments were performed on a fixed bed system, more appropriate in order to reduce the formation of secondary polymeric products that could be responsible for

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catalyst deactivation [12]. Phenol conversion and CO₂ production were monitored over 50 h.

2. Experimental

2.1. Preparation of the catalysts

Four 1%Ru/5%CeO₂-Al₂O₃ catalysts (mean particle diameter: 250 μm) were prepared by different methods: (i) **CCoImp** was prepared by co-impregnation of the support, with an aqueous solution of ethanol (50%), Ce(NO₃)₃·6H₂O and RuCl₃ using the dry soaking method; (ii) **CImp** was prepared by impregnation of the γ-Al₂O₃ support with Ce(NO₃)₃·6H₂O and then with an aqueous solution of RuCl₃ (two-step impregnation technique); (iii) **CPrec** was prepared by coprecipitation (at pH 10) from an aqueous solution containing the γ-Al₂O₃ support and appropriate amounts of Ce(NO₃)₃·6H₂O and RuCl₃; (iv) **CSurf** was prepared from a mixture containing 1 g of γ-Al₂O₃, 3 × 10⁻⁴ mol of Ce(NO₃)₃·6H₂O, 1 g of ethanol and 0.1 g of pluronic, that was calcined 4 h at 350 °C, and further impregnated with an aqueous solution of RuCl₃.

The samples were dried at 120 °C in oven, calcined at 400 °C for 12 h in air, and finally reduced at 400 °C under H₂ flow for 1 h. The reagents were reagent-grade, from Aldrich.

2.2. Characterization of the samples

BET surface areas were calculated from the nitrogen adsorption at -196 °C by using a Micromeritics ASAP 2010 surface analyser.

The ruthenium content of the samples was determined by Atomic Absorption (AA) using a Hitachi Z-8200 Spectrophotometer.

Hydrogen chemisorption was measured with a Micromeritics ASAP 2010 instrument equipped with a turbomolecular pump. Samples had been previously reduced in H₂ flow at 350 °C. After reduction, H₂ was removed from the metal surface with helium at 15 ml·min⁻¹ (30 min at 350 °C). The samples were subsequently cooled under the same He stream. The chemisorbed hydrogen was analyzed at 90 °C. The metal surface atoms were calculated assuming a stoichiometry H/Ru = 1 at the surface.

Powder X-ray Diffraction (XRD) patterns of the catalysts were obtained with a Siemens D5000 diffractometer by using nickel-filtered Cu Kα radiation. The patterns were recorded over 5 > 2θ > 85° range and compared to the JCPDS files to confirm phase identities. The patterns of the detected phase are: aluminum oxide (γ-alumina) (*d* = 1.40 Å (100), 1.97 Å (80), 2.4 Å (60), 4.6 Å (40) and 2.27 Å (30)); aluminum oxide hydroxide (boehmite) (*d* = 6.11 Å (100), 3.164 Å (65), 2.346 Å (55), 1.896 Å (30) and 1.860 Å (25)); cerium oxide (*d* = 1.631 Å (33), 1.913 Å (45), 2.705 Å (27), 3.12 Å (100)); ruthenium (*d* = 1.58 Å (25), 2.056 Å (100), 2.142 Å (35); 2.343 Å (40)).

The surface morphology of the catalysts was investigated by means of a scanning electron microscope (SEM) JEOL JSM6400 operating at an accelerating voltage in the range of 30–35 kV, a work distance between 7 and 9 mm and a magnification factor between 40,000 and 50,000.

Carbonaceous residues over the catalysts were eliminated by oxidation in a flow of synthetic air at 16 mL/min and 400 °C, followed by chromatographic detection of the produced CO₂ with a Konik 2000C equipped with an Alltech CTR I column and with a thermal conductivity detector.

2.3. Determination of catalytic activity and selectivity

Phenol oxidation was studied in aqueous medium, using a downflow packed bed reactor operated in the trickle regime. The experimental apparatus and the reaction procedure for the wet air oxidation were the same as those reported in a previous work [11].

A catalyst loading of 7.5 g of 1%Ru/5%CeO₂-Al₂O₃ and a phenol initial concentration of 5 g/L were used. Reaction experiments were carried out at 140 °C and 7 atm of oxygen pressure, with a gas flow of 0.46 L/min and a liquid flow of 1 mL/min. Liquid samples were withdrawn from the gas-liquid separator after steady state was reached. The samples were then analyzed for phenol content by a direct photometric method [23]. Chemical Oxygen Demand (COD) was determined by a closed reflux, colorimetric method, which is a rapid system for measuring the amount of oxygen consumption in the solution by K₂Cr₂O₇ [23]. Phenol conversion and CO₂ production were calculated as described by Massa et al. [11].

3. Results and discussion

Table 1 shows characterization results for the catalysts and the support. No significant differences in surface area

Table 1
Characterization of the catalysts and the support

Sample	Surface area (m ² /g)	XRD phase detected ^a	Ru content (%wt.)	Ru dispersion (%)
γ-Al ₂ O ₃	336	G	–	–
CImp				
Fresh	341	G + C + R	1.00	19
50 h	190	G + C + R + B	0.99	
CCoImp				
Fresh	310	G + C + R	0.97	17
Used 50 h	181	G + C + R + B	0.95	
CSurf				
Fresh	292	G + C + R	0.99	15
Used 50 h	145	G + C + R + B	0.99	
CPrec				
Fresh	298	G + C + R	0.89	2
Used 50 h	208	G + C + R + B	0.86	

^a Here, G stands for γ-alumina (γ-Al₂O₃); C for cerium oxide (CeO₂); B for boehmite (AlOOH) and R for ruthenium (Ru).

were detected among the support and the fresh samples. However, after several hours of reaction, the catalysts exhibited a pronounced reduction in superficial area. This could be due to the reaction conditions that may

induce some partial phase transformations on the gamma alumina support, as confirmed by XRD measurements.

The crystalline phases detected by X-ray diffraction for fresh and used catalysts are also summarized in Table 1.

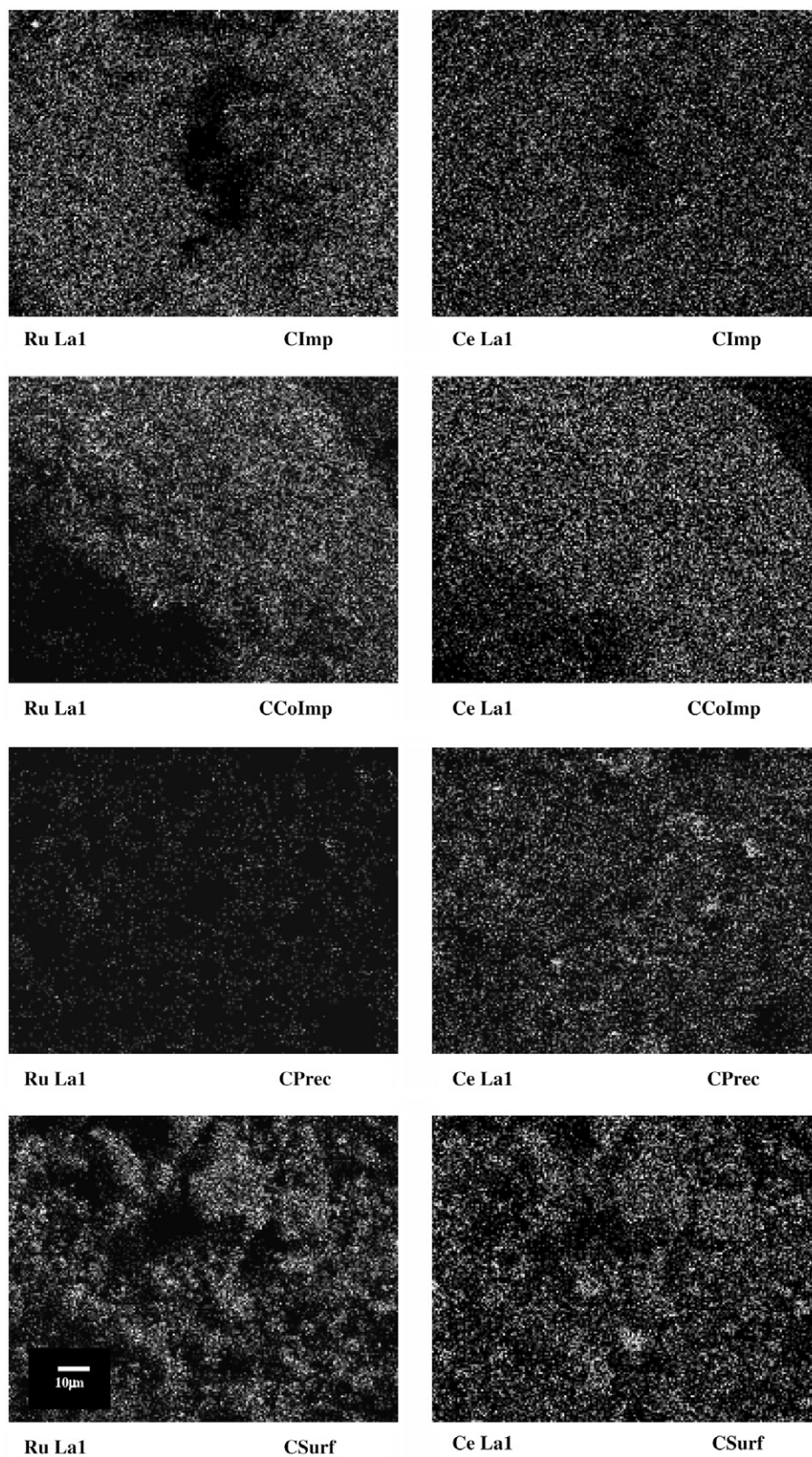


Fig. 1. SEM of dot mapping of different fresh catalysts: CSurf, CPrec, CImp and CCoImp.

The XRD patterns obtained for the fresh samples were similar: gamma alumina, cerium oxide and ruthenium phases were identified. For the used samples, the boehmite (AlOOH) phase was also detected. Previous works have reported that hot acidic conditions could provoke a phase transformation of the alumina to boehmite phase [24].

The dispersion of Ru particles on the surface of the catalysts was analyzed by hydrogen chemisorption and with SEM–EDX. Fig. 1 shows the dot mapping of Ru and Ce particles distribution on the surface of the catalysts. Impregnated catalysts (**CCoImp**, **CImp** and **CSurf**) presented the best Ru dispersion. This is in agreement with the results obtained from hydrogen chemisorption (Table 1). The **CImp**, **CCoImp** and **CSurf** fresh catalysts have dispersion values of 19%, 17% and 14%, respectively. On the contrary, a poor dispersion was observed for **CPrec** fresh catalyst (Fig. 1 and Table 1). This fact indicates that the preparation method has a strong influence on the metal dispersion. However, no significant differences were detected for Ce distribution on the surface of the samples.

The catalysts were tested in a TBR, at 140 °C and 7 atm of oxygen pressure. Blank runs were performed with γ -Al₂O₃ and 5%CeO₂- γ -Al₂O₃ support. Negligible levels of phenol conversion and CO₂ production were detected over γ -Al₂O₃. However, over 5% CeO₂- γ -Al₂O₃, phenol conversion and CO₂ production were in the order of 5%. Fig. 2 exhibits phenol conversion curves versus operation time, for all the samples. Initial phenol conversion levels were higher for **CCoImp** and **CImp** catalysts (near the 30%), while **CSurf** catalyst showed an initial conversion of around 25%. The catalyst prepared by the co-precipitation method (**CPrec**) showed only 6% of phenol conversion. These catalytic results are well correlated to the Ru dispersion (Table 1) as well as mapping distribution obtained from SEM–EDX (Fig. 1). The low dispersion observed for **CPrec** catalyst (2%), is responsible of its low catalytic performance. The main difference between these samples was that for **CCoImp**, **CImp** and **CSurf** the metallic precursor was incorporated by impregnation of the support, while for **CPrec** catalyst, the Ru

species were co precipitated with the ceria at pH 10. So, the preparation method strongly determines both the metal dispersion and the catalytic activity, due to the superficial distribution of the active sites. Probably, during the co precipitation of ceria and Ru at pH 10, the Ru particles may be covered by ceria blocking the access of the reactants. This could explain why the **CPrec** catalyst and CeO₂-Al₂O₃ support performed likewise. However, selectivity toward CO₂ production was, in all cases, nearly complete.

In order to test catalyst stability, the catalysts were used up to approximately 50 h. Table 2 presents phenol conversion as a function of reaction time. The three catalysts **CCoImp**, **CImp** and **CSurf** showed practically the same behavior: a significant phenol conversion decrease was observed, reaching blank runs conversion levels after 40 h of operation time. For catalyst **CPrec**, phenol conversion remained almost constant at a low value (near 5%).

As shown in Fig. 2, phenol conversion decreases continuously with reaction time, for catalysts **CCoImp**, **CImp** and **CSurf**. The CO₂ production exhibits a similar trend. According to Atomic Absorption measurements, the Ru content remained practically constant with usage (Table 1). So, deactivation can not be attributed to the loss of Ru species. Changes in the oxidation state of the metal should also be neglected; according to XRD results no oxidized species of ruthenium were registered. Deposition of carbonaceous solids is then considered: Pintar et al. [25] reported the presence of carbonaceous solids during phenol oxidation in a TBR operated at 130–150 °C with an oxygen partial pressure of 7 atm. Santos et al. [6] also mentioned the formation of deposits on the catalyst surface, promoting catalyst deactivation. In this case, the solids were formed by precipitation of the active phase (Cu⁺² species) with some reaction intermediates (oxalate ions).

In order to study the deactivation process, the used catalysts were oxidized at 400 °C in air (1 h). Chromatographic detection of CO₂ confirmed the presence of carbonaceous species, although no accurate quantification was completed. After reoxidation, catalysts were used in the

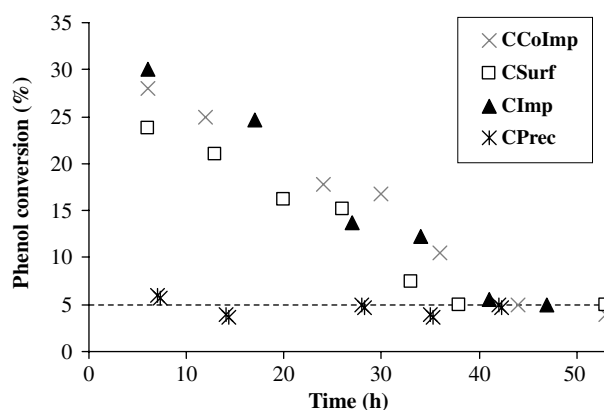


Fig. 2. Phenol conversion vs. operation time for the different catalyst. The dashed line represents the phenol conversion for the CeO₂-Al₂O₃ support ($T = 140$ °C; $P_{O_2} = 7$ atm; $Q_{liq} = 1$ mL/min; $m_{cat} = 7.5$ g).

Table 2
Phenol conversion and CO₂ production for different reaction times

Sample	Fresh catalyst		Oxidized catalyst	
	Used 7 h	Used 50 h	Used 7 h	Used 25 h
CCoImp				
Phenol conversion (%)	28	4	27	27
CO ₂ production (%)	25.4	4	27	25
CImp				
Phenol conversion (%)	30	5	14	5
CO ₂ production (%)	30	3	14	5
CSurf				
Phenol conversion (%)	24	5	24	11
CO ₂ production (%)	20	4	24	11
CPrec				
Phenol conversion (%)	6	4	5	5
CO ₂ production (%)	5	4	4	4

TBR for additional 25 h. Table 2 reports phenol conversions obtained after the oxidation process. As shown, phenol conversions increased with respect to the values obtained at 50 h of reaction. Furthermore, **CCoImp** and **CSurf** catalysts presented the best performance, with conversions close to those achieved with fresh samples. The removal of the carbonaceous deposits may increase the availability of the active species on the catalytic surface. Additionally, XRD patterns for reoxidized samples showed no boehmite phase peaks. Besides, the metal dispersion for reoxidized samples were very similar than for fresh catalysts. These effects would indicate that the main deactivation mechanism was related to the reversible deposition of carbonaceous solids on the active sites, combined with the evolution of the alumina support to the boehmite phase.

Efforts are in progress in order to study alternatives to improve catalyst stability, such as in situ oxidation of the catalyst during reaction.

4. Conclusions

- The 1%Ru/5%CeO₂-Al₂O₃ catalysts prepared by impregnation methods were active for the oxidation of phenol solutions in a TBR, at moderate temperature and oxygen pressure conditions (140 °C and 7 atm).
- For the sample prepared by coprecipitation, the Ru particles of the catalyst are not in direct contact with the reactants and the catalyst exhibited a lower performance, with similar conversion than the ceria support.
- A high selectivity towards CO₂ (above 90%) was found even for low phenol conversions.
- Stability tests showed that catalysts remain moderately active up to 30 h of use.
- Deactivation was mainly attributed to the deposition of reversible carbonaceous deposits on the active sites and to the formation of boehmite phase on the support. The last effect is favoured by the hot acidic reaction conditions.

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