

Catalytic Removal of Phenols with PtRu alloy/MoS₂ Nanoparticles Embedded in Hyper-Cross-Linked Polymers

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Here we report the performance in phenol heterogeneous catalytic wet air oxidation (CWAO) of polystyrene based hyper-cross-linked polymer (HCLP) synthesized with a new synthetic route. The resin loaded with nanoparticles of PtRu-alloy covered by MoS₂ nanosheets, prepared according to a "wet chemical" approach, was tested as catalyst in an experimental plant at atmospheric pressure. The results of the Gas Chromatography – Mass Spectroscopy (GC-MS) performed on the reaction solution after 5 h of reaction, evidenced the presence of acetic acid (retention time 14.17 min), which is one of the main biodegradable end products of phenol oxidation. At 19.95 min retention time is possible to evaluate the presence of non-reacted phenol. A phenol conversion up to 98 % was achieved.

Keywords: Catalytic Wet Air Oxidation, Hyper-Cross-Linked Polymers, Phenol, Nanocomposite

1. Introduction

Technological development has inevitably led to a strong increase in air, soil and water pollution and, consequentially, to a growing attention towards the environment. Among these pollutants, phenol and phenolic compounds are widely considered as very hazardous materials (Quintanilla et al., 2006), due to their chemical stability and oxidation resistance, that strongly affect risk of accumulation in the environment. The removal of phenolic compounds from water is typically carried out by several methods like sorption, extraction and membrane separation (Villegas et al., 2016), but none of these techniques lead to a complete and effective elimination of phenol and its derivatives. Conversion of this type of pollutants in non-hazardous or easily biodegradable compounds is assumed to be an attractive route for their removal and, among the various strategies, heterogeneous catalytic wet air oxidation (CWAO) is considered one of the best solutions (Castillejos-López et al., 2009). Key factors for the effective implementation of typical heterogeneous catalysts in this application are related to chemical stability and high metal content (Doluda et al., 2007): Pt-group metals are indeed the most active oxidation catalyst, but their use is limited by the high cost. Noble metal nanoparticles (NPs) due to the high specific area and additional phenomena related to the nanometer size, are pointed out to be good catalysts for various applications (Doluda et al., 2013), but are limited by the coalescence phenomena which can occur during the process, affecting catalyst dispersion (Campisi et al., 2016). To avoid this problem, active species are generally dispersed in the porous structure of high surface area supports, following the typical procedures of heterogeneous catalysis (Wang et al., 2014). Hyper-cross-linked polymers (HCLP), could represent the solution to the agglomeration problem: such materials are easily manufactured at low cost and have high chemical and thermal stability (Huang and Turner, 2018). Furthermore, they present a huge specific surface area (1000 – 1900 m²/g) (Castaldo et al., 2017a) with tunable pore size distribution. Indeed, among the different supports in a few number of cases HCLP have

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been also used (Doluda et al., 2013, 2007; Sulman et al., 2010). On the other hand, nanotechnology allows the control of catalyst NPs size, morphology, coupling between different active species and particle surface functionalization. Moreover, properly surface functionalized nanoparticles can be embedded in HCLP during the resin synthesis (Castaldo et al., 2017b), confining NPs in the hyper-cross-linked matrix, thus preserving nano-dimensions (Tan and Tan, 2017), reducing leaching phenomena and the amount of active species required because of total surface area exposed. Here we report the performance in phenol CWAO of PtRu-alloy covered by MoS₂ nanosheets NPs. The nanoparticles were prepared by a “wet chemical” approach (Sarno et al., 2016) and dispersed in a polystyrene based HCLP through a new synthetic route which allows to easily embed inorganic nanoparticles into the polymer matrix (Castaldo et al., 2017c). The effect of reaction time on the removal of phenols was investigated.

2. Experimental Section

2.1 Materials

Platinum (III) acetylacetonate (97 %), ammonium tetrathiomolybdate (> 99 %), Ruthenium (III) acetylacetonate (> 97 %), oleic acid, oleylamine, 1,2-hexadecandiol, 1-Octadecene, vinylbenzyl chloride (VBC, > 95 %, mixture of isomers, ~70 % meta + ~30 % para), *p*-divinylbenzene (DVB, 85 %, meta isomer ~10 wt %), 2,2'-azobis(2-methylproprionitrile) (AIBN, >98 %), FeCl₃ (> 97 %), phenol (> 99.5 %), 4-aminoantipyrine (AAP) potassium ferricyanide and sodium bicarbonate were purchased from Sigma Aldrich (Milan, Italy), and used without further purifications.

2.2 Synthesis of the nanoparticles

Platinum (III) acetylacetonate (1.271 mmol), ammonium tetrathiomolybdate (1.153 mmol) and ruthenium (III) acetylacetonate (0.753 mmol) were loaded into the reagent mixture, consisting of 20 ml of 1-octadecene, oleic acid (6 mmol), oleyl ammine (6 mmol) and 1,2-hexadecandiol (10 mmol) as reducing agent. The temperature was increased to 200 °C for 2 h and then the mixture was heated up to 285 °C for 1 h, in inert ambient (Sarno et al., 2015). After synthesis had been occurred, products were purified alternating ethanol and hexane washing and separating by centrifugation (Sarno and Troisi, 2017).

2.3 Synthesis of the nanocomposite

The hyper-crosslinked poly(divinylbenzene-co-vinylbenzyl chloride) based nanocomposite containing PtRu/MoS₂ nanoparticles was prepared through a two-step procedure.

DVB and VBC (molar ratio 2:98) were mixed with 5 phr of PtRu/MoS₂ nanoparticles. To ensure effective nanofiller dispersion, the mixture was sonicated for 50 min with a 500 W tip sonicator at 25 % power, with a 10 s/50 s ON/OFF cycle. Thereafter, 0.5 phr of AIBN was added, and the mixture was kept under stirring at constant temperature (80 °C) under nitrogen for 30 min. Polymerization was completed in an oven for 24 h at 80 °C. For comparison, neat poly(divinylbenzene-co-vinylbenzyl chloride) was prepared similarly. The obtained nanocomposite and polymer precursors were repeatedly washed with methanol, acetone and diethyl ether, and then dried in a vacuum oven at 40 °C for 24 h.

For the synthesis of the hyper-cross-linked systems, both precursors were swollen in 1,2-dichloroethane for 2 h, then the systems were cooled to 0 °C by means of an ice/water bath, FeCl₃ was added, and stirring was continued for 2 h. After that, the reaction flask was heated to 80 °C and kept at this temperature for 18 h. The obtained hyper-cross-linked resin and nanocomposite were washed with methanol and dried in a vacuum oven at 40 °C.

2.4 Characterization methods.

Bright field transmission electron microscopy (TEM) analysis was performed on the PtRu/MoS₂ NPs and the nanocomposite precursor by means of a FEI Tecnai G12 Spirit Twin (LaB₆ source) at 120 kV acceleration voltage. Before analysis, the PtRu/MoS₂ nanoparticles were dispersed in toluene by sonication and collected on holey carbon-coated copper grids, and ultrathin sections of the nanocomposite precursor were prepared with a Leica UC7 ultramicrotome (nominal thickness 100 nm) and deposited on TEM copper grids. TEM images were acquired by a FEI Eagle 4k CCD camera.

Surface area and pore size distribution analysis was performed on the hyper-crosslinked resin and nanocomposite by nitrogen adsorption measurements at 77 K, using a Micromeritics ASAP 2020 analyzer. Prior to the analysis all the samples were degassed at 120 °C under vacuum ($P < 10^{-5}$ mbar) and the measurements were performed using high purity gases (>99.999 %).

2.5 Catalytic tests

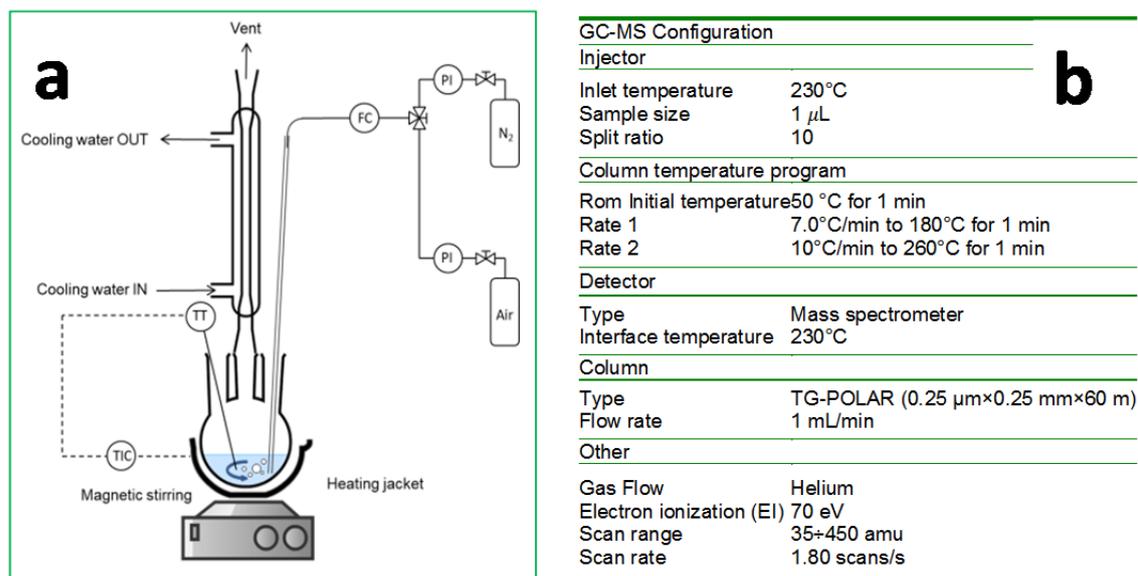


Figure 1. Scheme of experimental plant

Phenol catalytic/adsorption tests were performed on neat resin and the nanocomposite at 100 °C, phenol concentration 100 mg/L. 10 g/L (10 ml of initial solution) of the resin or nanocomposite was introduced into the experimental plant consisting of a glass reactor (50 ml), which was temperature controlled and fed with a constant air flow bubbling at 1 atm, a system for reflux was used to further control the experiments. Before each test nitrogen was blown into reaction environment. The temperature was kept at 95 °C. The phenol concentrations or UV-vis spectra were obtained using a Thermo-Scientific UV-Vis Evolution Q-60 spectrophotometer. Phenol concentrations were measured by colorimetric method. Absorbance was measured at 510 nm against a blank. Concentrations were measured using a previously recorded calibration curve ($\text{mg/ml of phenol} = 0,0195 \cdot \text{Abs} + 7\text{E}-05$ $R^2 = 0,9999$). Gas-chromatographic analyses were performed in a GC Focus Series (Thermo Scientific) coupled to a single quadrupole ISQ (Thermo Scientific) Mass Spectrometer. The method details are summarized in Figure 1b. Acylation of the reaction solutions was performed for analysis.

3. Results and discussion

3.1 Resin characterization

TEM image in Figure 2 allows to evaluate the morphology of the as prepared PtRu/MoS₂ nanoparticles (Figure 1a), which are covered by MoS₂ nanosheets (Sarno and Ponticorvo, 2017). The dispersion of the NPs in the polymeric matrix can be observed in Figure 1b. They exhibit an average dimension of 3.12 nm with a narrow size distribution (standard deviation = 0.78 nm), see Table 1. After the synthesis, which allows to “freeze” the mixture during the synthesis of the precursor, the nanoparticles result almost homogeneously dispersed in the polymer matrix. The X-ray diffraction pattern, not shown here, clearly evidences a slight up-shift of the peaks of pure Pt owing to the alloy formation with Ru. This phenomenon is due to the lattice contraction caused by the incorporation of Ru into the Pt lattice. Furthermore, in the diffraction pattern of PtRu/MoS₂ the peaks from MoS₂ nanostructures can be also recognized (Veeramalai et al., 2016).

Specific surface area and porosity of the hyper-cross-linked resin and nanocomposite were also measured by means of nitrogen volumetric gas adsorption. The nanocomposites and the neat resin exhibit a BET specific surface area (SSA) of 1370 m²/g and 1870 m²/g, respectively, and the nanocomposite shows a total pore volume about 20 % lower than the neat HCL resin. On the other hand, the pore size distribution in the two samples results substantially unmodified.

3.2 Catalyst performance

First of all, a test on the neat resin in the same operating conditions of the catalytic tests has been performed. The results are shown in Figure 3. The phenol adsorption tests performed on the neat resin evidence the capability of the system to adsorb more than 70 % of the phenol in 30 min. The UV-vis spectrum recorded at

120 min (Figure 4a) is practically superimposable to the spectrum of phenol recorded on the starting solution, confirming the absence of catalytic phenomena during adsorption. This result was confirmed by GC-MS evaluation, which shows a single peak, at 19.95 min retention time, attributable to phenol.

The UV spectra of the reaction mixture after 30 min and 300 min reaction are shown in Figure 4b. The absence of the typical phenol absorption band suggests the almost complete depletion of phenol. In particular, the spectrum at 30 min suggests the formation of quinones, see the scheme below in Figure 5. The spectrum at 300 min indicates the presence of acetic acid, which is one of the main end product of phenol oxidation (Doluda et al., 2013). The results of the GC-MS, performed on the reaction solution after 300 min of reaction, confirms the UV-vis evaluation, evidencing the presence of acetic acid (retention time 14.17 min), accounting for 98 % of the injected solution. At 19.95 min retention time is possible to evaluate the presence of non-reacted phenol 2 %. The results are more relevant, also if compared with literature, see Table 2, in light of the pressure conditions and small amount of noble metals used in our tests.

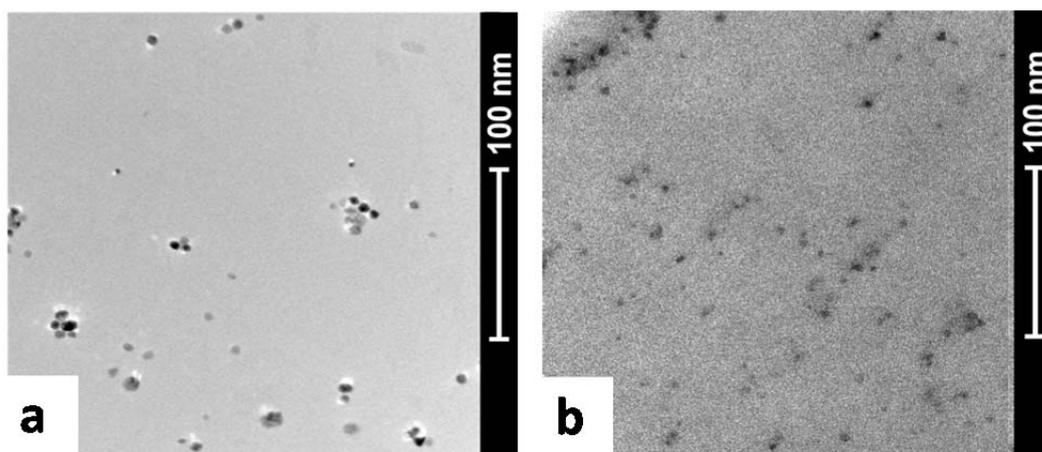


Figure 2. TEM images of PtRu/MoS₂ nanoparticles (a) and the precursor nanocomposite resin (b)

Table 1. Nanoparticle size distribution

Nanoparticles size distribution [nm]*	
Min	1.8
Max	5.09
Mean	3.12
St.dev	0.783

*on the base of Figure 2b

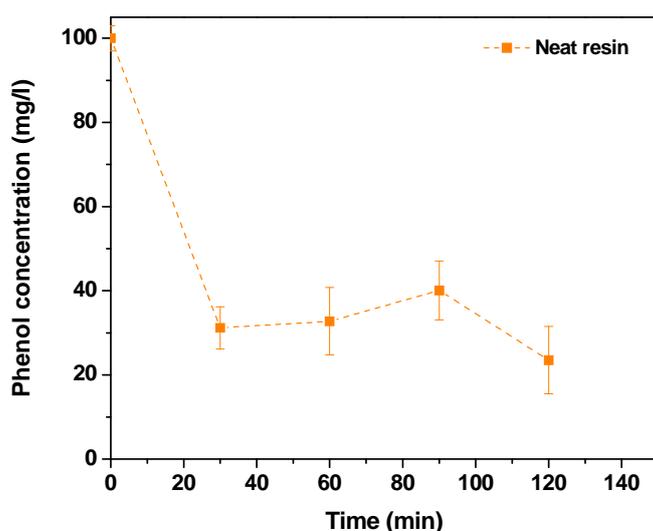


Figure 3. Residual phenol concentration after adsorption test on neat resin at 95 °C.

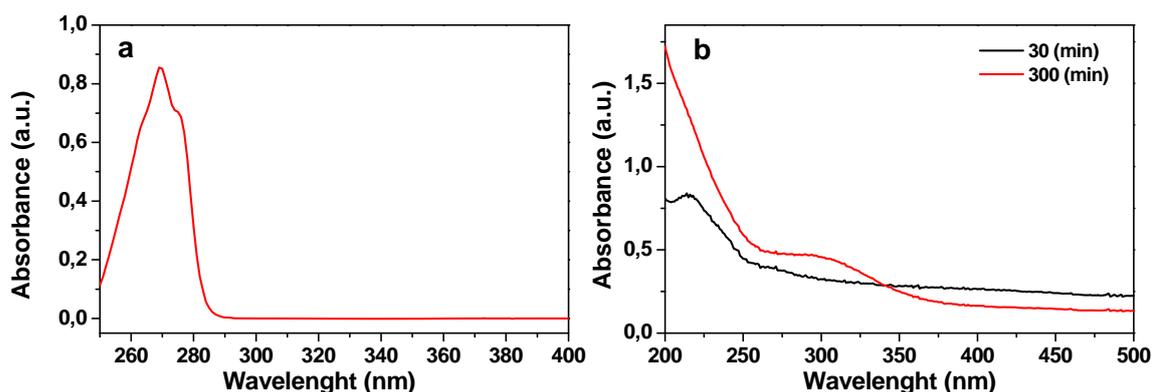


Figure 4. (a) UV-spectrum of the solution after 130 min test with neat resin at 95 °C (b) UV-spectra of the solutions after 30 min and 300 min tests with the nanocomposite at 95 °C.

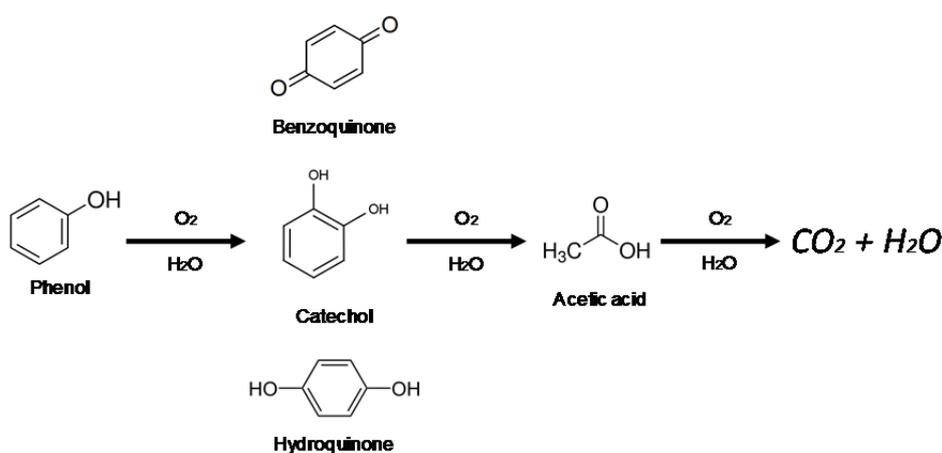


Figure 5. Scheme of phenol wet air oxidation.

Table 2. Literature survey of catalysts in wet air oxidation

Catalyst	Metal loading %	Reactor Volume (ml)	Reaction solution (ml)	mg _{cat} /mg _{phenol}	T [°C]	Time [min]	Pressure [MPa]	Phenol conversion	Reference
CWNTs;CFs; G	-	1000	500	0.0004	160	120	2.5 *	~100 %	(Wang et al., 2014)
Ru/ CFNs	1, 3	150	75	0.0008	180	360	5	80%	(Ayusheev et al., 2014)
CeO ₂	-	NR [§]	NR [§]	0.005	140 - 180	240	0.5 *	95%	(Lin et al., 2002)
Ru (CeO ₂)/AC	1.50	NR [§]	160	0.002	160	180	2 *	~100%	(Oliviero et al., 2000)
CeO ₂	-	NR [§]	NR [§]	0,0025	160	180	0.5- 1 *	93%	(Lin et al., 2003)
Metal/AC	0.50	1000	500	0.0005	200	120	0.42 *	~100%	(Cao et al., 2003)
Ru / HCL - PS	0.5 - 2.8	NR [§]	20	0.001	95	420	4.5 *	97%	(Doluda et al., 2013)
Pt / HCL - PS	0.11 – 5	NR [§]	20	0.0005	40 - 95	300	0.1 *	97%	(Sulman et al., 2010)
PtRu/MoS ₂	5	50	10	0.005	95	300	P atm	98%	This work

*pure oxygen; §Not Reported (NR)

4. Conclusions

Overall, the characterization evidences the quasi-complete successful removal of phenol and conversion in non-toxic products. The operating conditions (i.e. 95 °C; 1 atm; and 10 g/L, 5 wt. % of active species) indicate the excellent behavior of our nanocatalyst, due to the homogeneous dispersion of the catalyst in HCLP resin and the efficient contact with the reagent exposing their total surface area. The evaluation of carbon removal, i.e. CO₂ formation, and stability tests are in progress.

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