

Ruthenium Catalysts Supported on Multi Walled Carbon Nanotubes for the Catalytic Wet Air Oxidation of Aniline

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Oxidation of carbon multi-walled nanotubes (MWNTs) by nitric acid leads to the introduction of carboxylic groups that can be used to anchor a Ru metallic phase. Ruthenocene $[\text{Ru}(\text{C}_5\text{H}_5)_2]$, Ruthenium (1,5-cyclooctadiene, 1,3,5-cyclooctatriene) $[\text{Ru}(\text{COD})(\text{COT})]$, and Ruthenium trichloride $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ were used as precursors in the incipient-wetness (IW) and excess (EI) impregnation methods. The catalytic activity of the prepared materials in the wet air oxidation of aniline in aqueous solution, was found to depend on the type of Ru precursor in the following order: $[\text{Ru}(\text{COD})(\text{COT})] > \text{RuCl}_3 \cdot x\text{H}_2\text{O} > [\text{Ru}(\text{C}_5\text{H}_5)_2]$. The high aniline conversions observed (complete conversion in the case of the most active catalyst) are attributed to the high external surface area of the MWNTs ($S_{\text{BET}} = 175 \text{ m}^2/\text{g}$), which is compatible with end-closed nanotubes (zero micropore volume). This type of structure provides an efficient surface contact between the reactants (aniline) and the active sites, especially in the liquid phase where mass transfer limitations are very significant.

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Carbon nanostructures, nanotubes and nanofibers, the smallest organized form of carbon, have received an increasing scientific interest in the last decade, from a fundamental point of view as well as for their physical properties and for several of their prospective applications. Among all these applications the use of carbon nanotubes and nanofibers as catalyst support seems to be one of the most promising fields with large economical implications [1]. The results published to date indicate that nanostructured carbon materials can represent a new class of advanced materials for catalytic applications allowing the modification of the reaction rate and of the final product selectivity rendering the process more environmentally benign. At the nanometric scale particles exhibit singular physical and chemical properties between those of the smallest element from which they are composed and those of the bulk material [2]. The small size of carbon nanotubes and their modified composites greatly affects the surface structure and electronic properties of the material with enormous repercussion on the eventual catalytic properties [3].

The present communication reports one of the first uses of carbon multi-walled nanotubes (MWNTs) as catalyst support for an environmental application, the catalytic wet air oxidation of aniline in liquid-phase. The active phase consists of Ruthenium, which was deposited on the support by means of impregnation with liquid aqueous and non-aqueous solutions. In this method the support is wetted with the solution of the metal phase, then dried, and calcinated or reduced in order to produce a highly disperse metal phase.

The carbon nanotube surface has a hydrophobic nature, being extremely difficult to wet with aqueous solutions. Chemical oxidation of the surface by means of acidic treatments with nitric acid (HNO₃) was found to be a good method to develop a hydrophilic character on the surface, and simultaneously creating anchoring points for metal deposition [4]. The result of this type of treatment leads to carbon MWNTs containing –COOH surface groups. Further treatment with Na₂CO₃ leads to proton exchange and formation of and –COONa surface groups. The textural characterization confirms the absence of micropores and a BET surface area of 175 m²/g, which corresponds to the external surface area of the nanotubes.

Ruthenocene [Ru(C₅H₅)₂], Ruthenium (1,5-cyclooctadiene, 1,3,5-cyclooctatriene) [Ru(COD)(COT)] and Ruthenium trichloride RuCl₃.xH₂O were used as precursors and were dissolved in hexane, toluene ethanol or water respectively. The weight ratio of Ru-MWNT was controlled according to the targeted metal loading of 1% Ru. The catalysts were prepared using the incipient-wetness (IW) and excess (EI) impregnation methods. After impregnation the catalyst was dried for 12 or 24 h at over 100°C in an oven. The resulting agglomerates were ground and reduced in a furnace under flowing N₂/H₂. Finally the powdered material was cooled to room temperature in nitrogen atmosphere. The resulting catalysts were used in the liquid phase oxidation of aqueous aniline solutions.

Catalytic wet air oxidation (CWAO) is a liquid phase reaction in which an organic material undergoes degradation assisted by oxygen. It is an attractive treatment for wastewaters with a critical concentration of organic matter (chemical oxygen demand in the 5-50 g/L range), which makes other type of treatments inefficient [5]. Aniline and some of its azoic derivatives

are known to be very toxic and therefore of high negative impact if occurring in aqueous effluents [6]. The CWAO of aniline aqueous solutions (75 mL) was carried out in a stainless steel high-pressure reactor (Parr 4564) with temperature control. Standard conditions for a 2 hours run were a total pressure of 5.0 MPa, a temperature of 200 °C and 0.8 g of catalyst under continuous stirring (500 rpm). Liquid samples were periodically withdrawn from the reactor and analyzed by gas chromatography with a flame ionization detector (FID). The total organic carbon concentrations were obtained using a total carbon analyzer.

Comparing experiments 1 to 3 (Table 1) there is a clear correlation between the type of precursor and the activity, a decrease being observed in the order Ru(COD)(COT) > RuCl₃ > Ru(C₅H₅)₂, 100% aniline conversion being obtained after 45 min of reaction with the catalyst prepared with Ru(COD)(COT). On the other hand, the selectivity decreases in the order Ru(COD)(COT) > Ru(C₅H₅)₂ > RuCl₃.

In what concerns the influence of surface treatment, experiments 3 and 5 should be compared. It can be seen that the Ru/MWNT-COONa catalysts removed 98.3 % and 70.3 % of aniline and TOC, respectively, presenting higher activity than Ru/MWNT-COOH catalysts, with a correspondingly higher selectivity of 12%.

Table I. Catalytic wet air oxidation of aniline

Expts.	Precursor / Impregnation method*	D _M (%)	X _{Aniline} (%)	X _{TOC} (%)	S _{CO2} (%)
1. Ru/MWNT-COOH	[Ru(COD)(COT)] / EI	16.1	100.0**	80.8	80.8
2. Ru/MWNT-COOH	[Ru(C ₅ H ₅) ₂] / EI	4.5	76.0	59.2	77.9
3. Ru/MWNT-COOH	[RuCl ₃] / EI	11.2	89.9	53.7	59.7
4. Ru/MWNT-COOH	[RuCl ₃] / IW	10.5	94.3	66.8	70.8
5. Ru/MWNT-COONa	[RuCl ₃] / EI	16.9	98.3	70.3	71.5
6. Ru/AC	[RuCl ₃] / EI	10.2	100***	96.4	96.4
6. No catalyst	-	-	45.0	27.4	60.8
7. Bare MWNT-COOH	-	-	54.0	45.7	84.6

* EI: excess impregnation. IW incipient-wetness impregnation;

** At 45 minutes of reaction

*** At 100 minutes of reaction

The performance of the prepared catalysts reflects, among others, the potential capabilities of MWNTs as support material, providing not only for a significant metal dispersion, but also making available an efficient surface contact between the reactants and the active sites, especially in liquid phase, where mass transfer limitations are very significant.

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