Some aspects of the use of carbon nanotubes in catalysis

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Among the different types of supports used in heterogeneous catalysis carbon materials attract a growing interest owing to their peculiarities, which are mainly: i) resistance to acidic/basic media, ii) possibility of controlling, up to certain limits, their porosity and surface chemistry, and iii) easy recovery of precious metals by support burning, resulting in a low environmental impact. Since the early 90's carbon nanotubes (CNT) have generated a great effervescence in the scientific community due to their exceptional properties that make them suitable for many potential applications. Of course, such promising materials attract the interest of industrial groups that foresee a high economical impact in the near future. Among the main possible applications we will concentrate on the use of CNT in the field of catalysis [1], in this contribution. We will firstly give a critical analysis of the use of CNT in catalysis, focusing on expected breakthroughs. Then, case studies carried out in the authors' laboratories about the preparation of CNT-based catalysts and catalytic experiments performed on such systems will be presented.

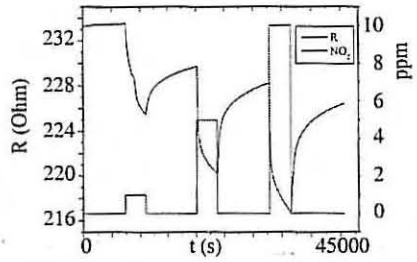
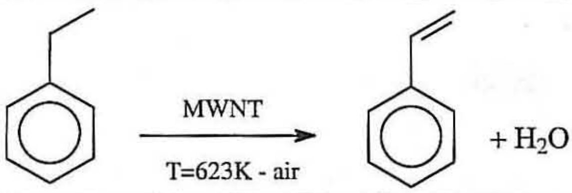
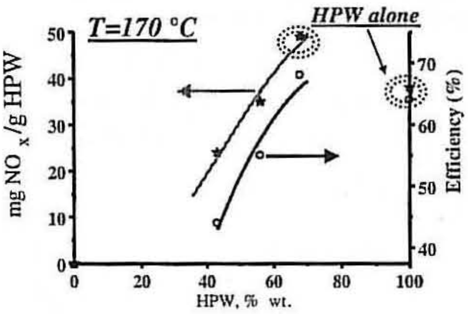
We will present some possible advantages that can be obtained by using CNT as catalysts or catalyst supports. We will particularly focus on CNT most interesting features in catalysis, such as structure, and electronic, adsorption, thermal and mechanical properties. Some considerations concerning the massive production and the price of these materials will be presented. The different kinds of catalytic reaction envisaged will be discussed.

The main preparation routes to CNT-based catalysts will be briefly introduced and we will insist on the necessity to activate CNT prior to their use as catalysts or supports. We will present some examples of characterization (TPD, XPS, BET,...) of activated CNT by means of nitric acid or oxygen treatments, and by mall milling. Such treatments lead to modification of specific surface area and/or surface chemistry. Then, the preparation of rhodium, platinum and ruthenium CNT-supported catalysts by grafting methods will be presented. In this case, activation of CNT followed by reaction with organometallic precursors as $[RhCl(CO)_2]_2$, $[Pt(Me)_2(COD)]$ and [Ru(COD)(COT)] allow the preparation of highly dispersed catalysts. Mean particle sizes of 2-3 nanometers have been measured for 1% w/w Pt, Ru or Rh catalysts.

The reactivity of activated multi-walled carbon nanotubes (MWNT) or MWNT-supported catalysts were investigated for different applications. We have evaluated the gas sensing behaviour of resistance-based sensors employing MWNT as the active sensing element and NO_2 as probe molecule. Oxidative dehydrogenation of ethylbenzene (EB) to styrene (ST) was carried out on MWNT. The possibility of using MWNT as supports for the heteropolyacid $H_3PW_{12}O_{40}\cdot 6H_2O$ (HPW) in order to adsorb NO_x from lean mixtures was explored.

Finally we also studied the liquid phase catalytic wet air oxidation of aniline (An) on platinum and ruthenium MWNT-supported catalyst . The main results are summarized on the following Table.

Table: Catalytic applications of MWNT

<table>
<tr><th>Application</th><th>Main Results</th></tr>
<tr><td>MWNT + 1 ppm NO_2</td><td>
</td></tr>
<tr><td>
</td><td>
<table>
<tr><th>Cat.</th><th>X_{EB} (%)</th><th>S_{ST} (%)</th><th>a_{EB} (10^3 $\mu molm^{-2}s^{-1}$)</th></tr>
<tr><td>MWNT</td><td>19</td><td>59</td><td>45</td></tr>
<tr><td>MWNT-OX</td><td>27</td><td>67</td><td>60</td></tr>
</table></td></tr>
<tr><td>HPW/MWNT + NO/NO_2
↓
[$H^+(NO_2^-,NO^+)$]-HPW/MWNT</td><td>
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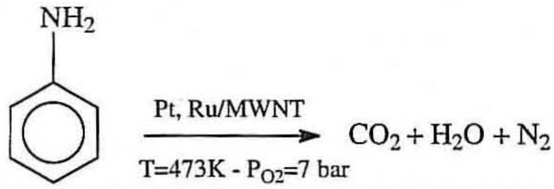
<tr><td>
</td><td>
<table>
<tr><th>Cat.</th><th>X_{An} (%)</th><th>X_{TOC} (%)</th><th>S_{CO2} (%)</th><th>t (min)</th></tr>
<tr><td>Ru/MWNT</td><td>100</td><td>81</td><td>81</td><td>45</td></tr>
<tr><td>Pt/MWNT</td><td>99.4</td><td>78</td><td>79</td><td>60</td></tr>
</table></td></tr>
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For some reactions, a comparison of the catalytic performance was made between MWNT- and activated carbon based systems. The observed results confirm the potential of MWNT as catalysts or supports for the development of new highly active heterogeneous catalytic systems.

[1] Ph. Serp, M. Corrias, Ph. Kalck, *Appl. Catal. A*, **2003**, 253, 337-358.