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Supported C-scorpionate vanadium(IV) complexes as reusable catalysts for xylene oxidation

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Dedication ((optional))

Abstract: C-scorpionate vanadium(IV) [VO$_x$Cl$_{3-x}${κ^3-RC(pz)$_3$}] [pz = pyrazol-1-yl; x = 0, R = SO$_3$ (**1**); x = 1, R = CH$_2$OH (**2**) or CH$_2$OSO$_2$Me (**3**)] complexes supported on functionalized carbon nanotubes (CNT) are the first V-scorpionate catalysts used so far for the neat oxidation of *o*-, *m*- or *p*-xylene, with TBHP (70% aqueous solution), to the corresponding toluic acids (main products), tolualdehydes and methylbenzyl alcohols. Remarkably, a *p*-toluic acid yield of 43% (73% selectivity, TON = 1.34 × 10^3) was obtained with **2**@CNT in a simple microwave-assisted mild oxidation procedure, using a very low catalyst charge (3.2 × 10^{-2} mol% *vs*. substrate). Further, this occurred in the absence of any bromine source, what is significant towards the development of a greener and more sustainable process for xylenes oxidation. Moreover, catalysts reuse with preservation of their activity was found for up to six consecutive cycles. The effects of reaction parameters, such as reaction time, temperature, amount of catalyst or type of heating source, on the performance of the above catalytic systems are reported and discussed.

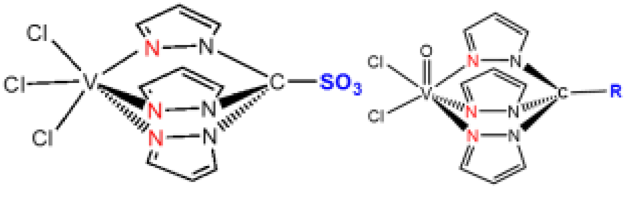
Introduction

The selective catalytic oxidation of hydrocarbons is an important route for preparing commodities in chemical industry worldwide. Large scale terephthalic acid production from the oxidation of *p*-xylene is a very important process in polyester industry[1] as it is manly used in polyethylene terephthalate (PET) manufacturing, a polymer that finds huge use in fibers, films and plastic products. Currently, oxidation of *p*-xylene is conducted in a homogeneous Co/Mn catalytic system in the presence of the highly corrosive bromide dissolved in aqueous acetic acid (AMOCO process).[1a] Despite the very high conversions of the reactant attained in the AMOCO process, and some recently reported[2] homogeneous greener alternatives (*e.g.*, a spray process,[3] the use of water[4] or supercritical CO$_2$[5] as solvents or of additives such as *N*-hydroxyimides and guanidines[6]), as well as heterogeneous ones (*e.g.*, Co/Mn cluster complexes encapsulated in zeolite Y,[7] Pd, Sb and Mo supported on TiO$_2$,[8] or AuPd alloy nanoparticles[9]), the development of a halogen free, low cost, sustainable and still highly efficient catalytic system to produce terephthalic acid is needed. Moreover, all heterogeneous systems described so far[1a, 2a] lack activity compared to the homogeneous initiator system and the active metal compounds are leached in the reaction medium.

Although benzylic oxidations can be catalyzed by vanadium species,[10] the oxidation of xylenes using vanadium complexes as catalysts, either in homogeneous environment or heterogeneized, has not been previously reported, what prompted us to investigate the catalytic activity of such metal in the above oxidation reaction.

On the other hand, the use of metallic complexes with C-scorpionate poly(pyrazol-1-yl)methane ligands as homo- or heterogeneous oxidation catalysts has experienced significant advances in the last years.[11] The tripodal C-scorpionate ligand, bearing three pyrazolyl moieties (via their N atoms) can assist proton-transfer steps that are believed to be involved in key catalytic processes.[12]

In this work, we aim to use the tripodal C-scorpionate vanadium(IV) [VO$_x$Cl$_{3-x}${κ^3-RC(pz)$_3$}] [pz = pyrazol-1-yl; x = 0, R = SO$_3$ (**1**);[13] x = 1, R = CH$_2$OH (**2**)[14] or CH$_2$OSO$_2$Me (**3**)[15]] complexes (Fig. 1) that have proven their efficiency as catalysts for the partial oxidation of cycloalkanes to the corresponding cyclic alcohols and ketones, but were not used for other substrates.



1

2 R = CH$_2$OH
3 R = CH$_2$OSO$_2$Me

Figure 1. Tripodal C-scorpionate vanadium(IV) [VCl$_3${κ^3-SO$_3$C(pz)$_3$}] (**1**) (pz = pyrazol-1-yl) and [VOCl$_2${κ^3-RC(pz)$_3$}] [R = CH$_2$OH (**2**) or CH$_2$OSO$_2$Me (**3**)] catalysts.

Moreover, in order to combine the useful properties of these homogeneous catalysts with the advantages of heterogeneous systems (*e.g.*, recyclability and practical, easy workups) we have chosen to support them on functionalized carbon nanotubes, according to the already established protocols.[16]

In addition, the use of microwave (MW) radiation as an alternative energy source, eventually enhancing product yield

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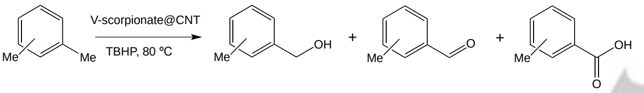
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) and selectivity as well as being more energy efficient and economical in comparison to conventional heating methods,[17] is appealing for the implementation of sustainable chemical processes. However, the application of MW irradiation in alkyl substituted aromatics functionalization is still an unexplored field.[18]

To our knowledge, this is the first time that the successful use of a C-scorpionate vanadium catalyst for the oxidation of xylenes is reported.

Results and Discussion

p-Xylene and its *o*- and *m*- isomers were successfully activated at one methyl group (Scheme 1) using C-scorpionate vanadium(IV) [$VO_xCl_{3-x}\{\kappa^3\text{-}RC(pz)_3\}$] [pz = pyrazol-1-yl; x = 0, R = SO_3 (**1**); x = 1, R = CH_2OH (**2**) or CH_2OSO_2Me (**3**)] complexes supported on surface functionalized carbon nanotubes (CNT) as catalysts and aqueous *tert*-butyl hydroperoxide (TBHP) as oxidant, leading to the formation of the corresponding toluic acids (main product), tolualdehydes and methylbenzyl alcohols. The catalytic results obtained are displayed in Table S1 (ESI).



Scheme 1. Oxidation of *o*-, *m*- or *p*-xylenes to the corresponding methylbenzyl alcohols, tolualdehydes and toluic acids.

Remarkably, a yield of 43% of *p*-toluic acid (TON = 1.34×10^3) was achieved in the presence of the hybrid catalyst **2**@CNT, prepared by heterogeneization of [$VOCl_2\{\kappa^3\text{-}HOCH_2C(pz)_3\}$] (**2**, pz = pyarazolyl) at carbon nanotubes oxidized with HNO_3 and subsequently treated with NaOH (CNT), after 12 h of microwave irradiation of *p*-xylene in acidic media (Fig. 2).

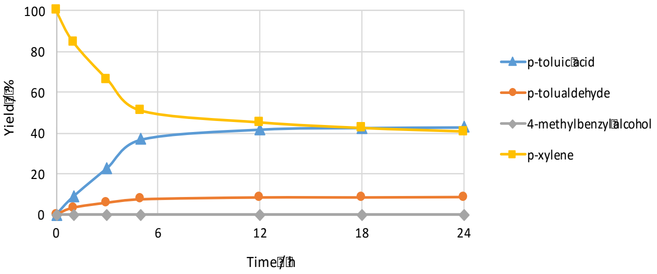
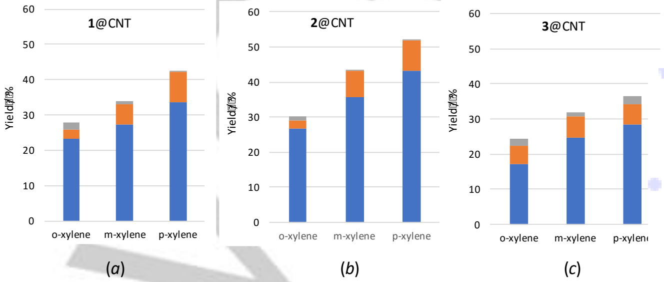


Figure 2. Effect of reaction time on the reaction yields of MW-assisted *p*-xylene oxidation with TBHP, at 80 ºC, catalyzed by **2**@CNT, in the presence of HNO_3.

The *o*- and *m*-xylenes were also mainly converted to the corresponding acids by the above procedure, although in slightly lower yields. Under the optimized conditions, catalysts performance for all the xylenes followed the trend: **2**@CNT > **1**@CNT > **3**@CNT (Table S1, Fig. 3). This follows the amount of supported V catalyst obtained in each hybrid material (Fig. S2).

The immobilization of C-scorpionate vanadium complexes **1** – **3** on the functionalized carbon nanotubes could occur via with the oxygenated functional groups (carboxylate or phenolate) of the CNT, with possible formation of a covalent VO bond, upon displacement of a chloride ligand[16b,19] or by replacement of one of the coordinated pyrazolyl arms of the C-scorpionate ligands, which thus would change from the trihapto to a dihapto coordination mode. This tri-/bi- interchange is a known[11] feature of these ligands, believed to be the core of the chemical versatility of metal complexes of this kind and essential for their catalytic applications.



(*a*) (*b*) (*c*)

Figure 3. Products yields obtained for the MW-assisted oxidation of xylenes (■ toluic acid, ■ tolualdehyde and ■ methylbenzyl alcohol) with TBHP, at 80 ºC catalyzed by (*a*) **1**@CNT, (*b*) **2**@CNT and (*c*) **3**@CNT, in the presence of HNO_3

The reaction can proceed, in the absence of added solvents, at the desired temperature (typically 80 ºC) using a conventional, heating mode (oil bath), but the preferred procedure is the microwave-assisted one (see Table S1 and Fig. 4 for the formation of *m*-toluic acid catalyzed by **1**@CNT). In fact, the used low power MW-assisted irradiation, that provides rapid initial heating and enhanced reaction rates, leads to a much more efficient synthetic method than conventional heating under open atmosphere or non-pressurised refluxing, allowing the attainment of significant higher yields in much shorter times (*e.g.*, 31% yield of *m*-toluic acid was obtained after 5 h of MW reaction catalyzed by **1**@CNT, whereas only 7.5% of *m*-toluic acid was formed under the same conditions but using an oil bath, Fig. 4).

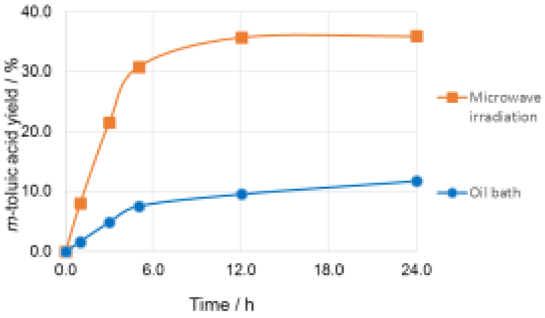


Figure 4. Effect of reaction time and heating method, oil bath (●) or microwave irradiation (■), on the yield of *m*-toluic acid obtained from oxidation of *m*-xylene with TBHP at 80 ºC, catalyzed by **1**@CNT.

Although the activation at one methyl group of xylenes occurs in the absence of any additive, the presence of acid enhances it (Fig. 5). In particular, the use of nitric acid as co-catalyst

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allowed to achieve the highest yields of the desired toluic acids (Table S1 and Fig. 5 for *m*-xylene oxidation). Moreover, the activation at one methyl group of xylenes is significantly enhanced by the heterogeneization of the vanadium catalysts at the functionalized carbon nanotubes (compare the results for **1** and **1**@CNT, Fig. 5).

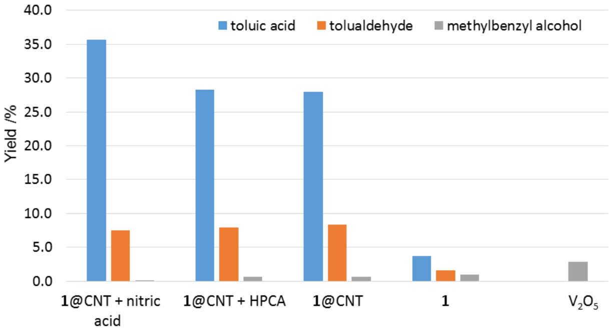

Figure 5. Products yields for the MW-assisted net oxidation of *m*-xylene catalyzed by different homo- and heterogeneous catalysts. HPCA = pyrazine carboxylic acid.

The high yields of toluic acids achieved under mild conditions with very low loadings of V-catalyst (see Fig. S1 for optimization of reaction conditions) along with the selectivity found for the activation of one methyl group of xylenes (no hydroxylation of the aromatic ring was observed) indicate a remarkable activity and selectivity of these heterogeneous catalytic systems based on the C-scorpionate vanadium(IV) complexes **1** – **3** supported on functionalized carbon nanotubes. Note that the use of a common V(V) oxide did not afford toluic acid or even tolualdehyde (Fig. 5), suggesting a significant role for the C-sorpionate ligands at our catalysts (see above). In addition, the presence of excess of oxidant also did not lead to more oxidized species under the tested conditions (see Fig. S3).

Therefore, and in contrast to previous studies, a notable catalytic activity of the C-scorpionate V(IV) complexes **1** – **3** heterogeneized on functionalized CNT is observed under mild conditions and in the absence of any bromine source, what is significant towards the development of a safer and more sustainable process for *p*-xylene oxidation. In fact, the present catalytic systems, in comparison with the Amoco process[1a, 2a] have the advantages of not requiring the use of corrosive HBr that leads to a hazardous reaction[20] and requires a reactor costly to build and maintain, and of avoiding the use of acetic acid solvent.

Another important advantage of their present systems is the possibility of the catalyst being recycled and re-used. Recycling of the best catalyst, **2**@CNT, was tested up to six consecutive cycles. On completion of each stage, the products were analyzed and the catalyst was recovered by filtration, thoroughly washed with acetonitrile, and then reused for a new set of xylene oxidation experiments. Fig. 6 shows the recyclability of the system **2**@CNT.

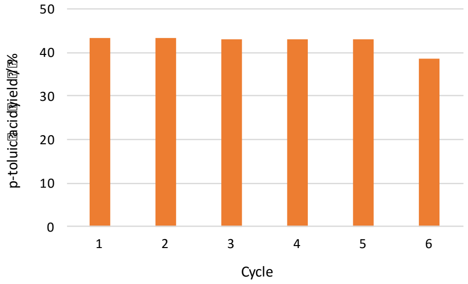

Figure 6. Effect of the catalyst recycling on the yield of *p*-toluic acid obtained by oxidation of *p*-xylene catalyzed by **2**@CNT.

The morphology of catalysts **1**-**3**@CNT before the oxidation reaction and after the 6th consecutive cycle is different, as illustrated by SEM (Fig. S3). Moreover, vanadium leaching, confirmed by EDS (Fig. S3), from the support surface may be responsible for the observed yield decrease after that cycle. For example, a drastic decrease of *p*-toluic acid yield (from 38.5%, Fig. 6) to values similar to those obtained by **2** (not supported, 12.3%), was observed in the 7th consecutive oxidation cycle catalyzed by **2**@CNT.

The catalytic reaction is believed to proceed via a radical mechanism, since a marked product yield decrease occurs in the presence of a radical trap, such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). Methylbenzyl radical ($TolCH_2^{\bullet}$) can be formed upon oxidation of xylene by V^V, and its reaction with O_2 leads to the peroxy radical $TolCH_2OO^{\bullet}$, which can account for the formation of the various products, as reported for other metal catalysts (*e.g.*, of Co^{III}).[1a, 21, 22]

Conclusions

C-scorpionate vanadium(IV) complexes were supported on functionalized carbon nanotubes and used for the first time in the neat oxidation of *o*-, *m*- or *p*-xylene, to the corresponding toluic acids (which were the main products), tolualdehydes and methylbenzyl alcohols. A *p*-toluic acid yield of 43% (73% selectivity, TON = 1.34 × 10^3) was obtained with **2**@CNT in a simple microwave-assisted mild oxidation procedure with TBHP, in the absence of a bromine source. This is quite an achievement towards the development of greener and more sustainable processes for xylenes oxidation. Moreover, catalysts recycle was possible up to five consecutive cycles without loss of activity. After the 6th cycle, V leaching is observed and activity starts to decrease.

Experimental Section

Materials and Instrumentation

All the reagents were purchased from commercial sources and used as received. Solvents were dried when necessary, by refluxing over the appropriate drying reagents and distilled under nitrogen prior to use. The scorpionate vanadium(IV) complexes $[VCl_3\{\kappa^3\text{-}SO_3C(pz)_3\}]$ (**1**),[12] $[VOCl_2\{\kappa^3\text{-}HOCH_2C(pz)_3\}]$ (**2**)[13] and $[VOCl_2\{\kappa^3\text{-}MeSO_2OCH_2C(pz)_3\}]$ (**3**)[14] were synthesized according to reported procedures and characterized accordingly.

^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker Avance II + 300 (UltraShield^{TM} Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively, at ambient temperature. The chemical shifts are reported in ppm using tetramethylsilane as an internal reference.

Infrared spectra (4000–400 cm^{-1}) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. Far infrared spectra FIR (400-200 cm^{-1}) were recorded on a Vertex 70 spectrophotometer in CsI pellets.

Elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico.

SEM and EDX analyses were carried out on a scanning electron microscope JEOL 7001F with Oxford light elements EDS detector and EBSD detector.

Reactions under microwave (MW) irradiation were performed in a focused Anton Paar Monowave 300 reactor fitted with a rotational system and an IR temperature detector, using a 10 mL capacity reaction tube with a 13 mm internal diameter.

GC-MS analyses were performed using a Perkin Elmer Clarus 600 C instrument (He as the carrier gas), equipped with two capillary columns (SGE BPX5; 30 m × 0.32 mm × 25 mm), one having an EI-MS (electron impact) detector and the other one with a FID detector. The temperature of injection was 330 ºC. The initial temperature (50 ºC) was raised at 5 ºC/min to 300 ºC. Reaction products were identified by comparison of their retention times with known reference compounds, and by comparing their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

Support synthesis

Multi-walled carbon nanotubes (CNT) NC3100 from Nanocyl^{TM} were treated in reflux with 75 mL of a 5 M nitric acid solution per gram of carbon material, for 3 h, then separated by filtration and washed with deionized water until neutral pH, similarly to what is described in literature.[15, 19] The obtained material was further treated with 75 mL of a 20 mM NaOH aqueous solution (per gram of carbon material) in reflux for 1 h, as in literature.[15, 19b, 20] This material was also separated by filtration and washed until neutral pH.

Heterogenisation procedure

The V complexes were anchored onto CNT (0.15 g) through dissolution in 25 mL of distilled water with continuous stirring for 24 h, in order to achieve 0.2 mmol V per gram of CNT. Afterwards, the material was deposited by gravity and separated by filtration, washed with water and methanol, and dried overnight at 40 ºC, under vacuum.

Metal loading determination

The loading of V was determined by atomic absorption spectroscopy (AAS) using a Unicam 939 atomic absorption spectrometer and a V hollow cathode lamp.

Catalytic tests

In a typical MW-assisted reaction, 2.5 mmol of xylene, 5 mmol of *tert*-butyl hydroperoxide (TBHP, 70% aq. solution) and vanadium catalysts **1-3**@CNT (0.16 – 0.80 μmol of V supported at CNT, 6.4×10^{-3} – 3.2×10^{-2} mol% *vs*. substrate) were introduced into a 10 mL glass vessel. In the experiments with HNO_3 (65%, 1.6 – 8.0 μmol) this acid was added immediately before the addition of the catalyst. The mixture was subjected to microwave irradiation at the desired temperature for the selected time at 600 rpm stirring speed. At the end of the reaction, the mixture was cooled down to r.t., the organics extracted with 2.5 mL of acetonitrile and identified by GC-MS. The V-catalysts were separated by filtration, washed with acetonitrile, dried with compressed air and reused in subsequent oxidation cycles.

For comparison, xylene oxidation reactions were performed in round bottom flasks under the same reaction conditions but using an oil bath as heating source (up to 3 mL total volume).

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Keywords: xylene • oxidation • C-scorpionate • carbon nanotubes • vanadium

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Layout 1:

FULL PAPER

C-scorpionate vanadium(IV) complexes supported on functionalized carbon nanotubes (CNT) are the first V-scorpionate catalysts used so far for the neat oxidation of *o*-, *m*- or *p*-xylene, with TBHP (70% aq. solution), Remarkably, a *p*-toluic acid yield of 43% (73% selectivity, TON = 1.34 × 10^3) was obtained in a simple microwave-assisted mild oxidation procedure.

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Supported C-scorpionate vanadium(IV) complexes as reusable catalysts for xylene oxidation

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