UNIVERSITA’ DEGLI STUDI DI PARMA

DOTTORATO DI RICERCA IN

"SCIENZE CHIMICHE"

CICLO XXX

Supported sulphonic acids: solid catalysts for eco-compatible oxidation reactions

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1 Green methods in organic chemistry

1.1 General introduction

In recent years the need to reduce production costs and the increasing regulations in pollution prevention prompted industries and academia to revise old processes in order to obtain safer and cleaner procedures for fine chemical and pharmaceutical synthesis.

This trend towards what has become known as "Green Chemistry" [1-3] or "Sustainable Technology" necessitates a paradigm shift from traditional concepts of process efficiency, that are mostly based on chemical yield, to something that assigns economic value to eliminating waste at source and avoiding the use of toxic and/or hazardous substances.

Novel processes should encounter several requirements such as high chemo-, regio- and stereoselectivity, one pot or multi-component reactions instead of multi-step procedures, the use of non-toxic solvents or solvent-free reactions, the elimination of toxic and/or harmful reagents, the improvement of atom economy, etc.

A reasonable working definition of green chemistry can be formulated as follows: "*Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products*".

An alternative term that is currently utilized by the chemical industry is Sustainable Technology. Sustainable development has been defined as [4]: "*meeting the needs of the present generation without compromising the ability of future generations to meet their own needs*".

In order to reach the goal of Green Chemistry and Sustainable Technology, organic synthesis should take advantage from new different methods. This work mainly deals with the application of the heterogeneous catalysis with special attention into oxidative processes.

1.2 Sol-Gel process

The sol-gel processes constitutes an important part of so-called “soft chemistry”. The sol-gel process has many technological applications [5-6], such as production of coating with specific optical properties, organic-inorganic hybrid materials supports for catalysts and culture media in biology.

In this paper, most of the catalysts presented were prepared employing the Sol-Gel process.

The success of the experiments is highly sensitive to many parameters, and hence the rapid manufacture of “nice” materials is not at all straightforward.

1.2.1 General considerations about the Sol-Gel process

Basic chemical reactions

The principle of the sol-gel process [7-8] is rather simple: a network of an oxide is progressively built through inorganic polymerization reactions at room or moderate temperature. Depending on the regulatory of the macromolecular structure obtained, crystalline (e.g. quartz) or amorphous (e.g. glass) materials may be prepared. The usual molecular precursors are metal-organic compounds such as alkoxides $M(OR)_n$, where M is a metal or a metalloid and R is an alkyl group ($R = CH_3$, C_2H_5, etc.). For example, tetraethylorthosilicate (TEOS) is commonly used in the sol-gel synthesis of silica and glasses. Such chemicals are dispersed in a solvent (usually organic, e.g. ethyl alcohol) and react according to the well-known steps in polymer chemistry:

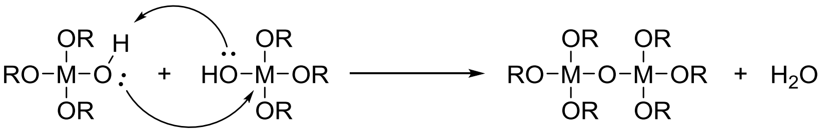
- *Initiation*. Corresponds to the hydrolysis of the alkoxides:

$$M(OR)_n + x\,H_2O \rightleftharpoons M(OR)_{n-x}(OH)_x + x\,ROH$$

The reactive bond M-OH, which is necessary for the continuation of the reaction, is formed during this step.

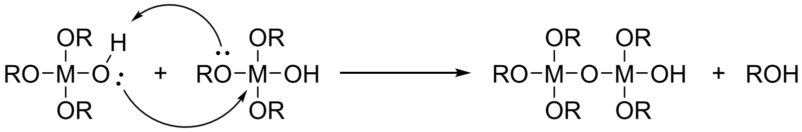
- *Propagation*. Condensation of the hydrolyzed species, with formation of bridging oxygens, according to two possible mechanisms:

<u>oxolation</u>, which corresponds to a dehydration (i.e., the leaving group is H_2O)



$$RO{-}M(OR)_2{-}OH + HO{-}M(OR)_2{-}OR \longrightarrow RO{-}M(OR)_2{-}O{-}M(OR)_2{-}OR + H_2O$$

or <u>alcoxalation</u>, which corresponds to a dealcoholation (i.e., the leaving group is ROH)



$$RO{-}M(OR)_2{-}OH + RO{-}M(OR)_2{-}OH \longrightarrow RO{-}M(OR)_2{-}O{-}M(OR)_2{-}OH + ROH$$

At the end, every oxygen is bridging and hence a pre and highly homogeneous oxide network is obtained. Depending on the chemical nature of the precursors, the final material contains one or several metal elements.

1.2.2 Sol-Gel transition

Between the starting solution and the final solid, several intermediate steps in which sols or gels are formed occurs, thus giving the name of the sol-gel process. The polycondensation of the precursors leads to bigger and bigger molecular species. Firstly, a sol (a colloidal suspension of solid particles in a liquid) is obtained. Since the polymerization reactions are going on, the particles grow and coalesce to form clusters which continuously increase in size. After a time, reaction mixture become a gel (an alcolgel, if the reactions take place in an alcohol), that is to say a semisolid system comprising two phases, solid and fluid, embedded in each other in such a way that the pores of the solid (filled with solvent) are of colloidal dimensions.

The gel point that marks the sol-gel transition may be identified by continuously recording the viscosity (η) during the synthesis.

Next, the gel strengthens progressively as the residual isolated clusters make bonds with the developing network: this phenomenon is usually called aging. The growing number of bonds and the occurrence of dissolving-reprecipitation reactions make the elastic modulus increase with time. The gel has now suitable features to be dried with the lowest number of cracks.

1.2.3 Drying the Gel

The alcolgel represents the penultimate stage of the process. Depending on its thermal treatment, various materials can be obtained. The solvent can be evacuated according to two methods.

1) *Evaporation*. Owing to the capillary forces exerted by the solvent, elimination of the solvent induces the shrinkage of the gel. A xerogel is thus obtained, which has a volume 5 to 10 times lower than that of the starting alcolgel. A subsequent thermal treatment may convert it into a dense ceramic.
2) *Supercritical evacuation*. The alcolgel is placed in an autoclave and brought to temperature and pressure higher than Tc and Pc respectively. In these conditions, in the presence of a supercritical fluid, liquid-gas menisci and hence capillary stresses vanish. After the critical point, the temperature is kept constant while the supercritical fluid is evacuated by decreasing the pressure.

Thus the solvent is extracted in such a way that the solid phase is dried without undergoing any volume change. An extremely light material, called aerogel, results; its porosity may be as high as 98%. Again, appropriate thermal treatment leads to more dense materials.

1.2.4 Applications of the Sol-Gel process

Owing to the high costs involved (a glass made by sol-gel is about 100 times more expensive than a classical one), the use of the sol-gel process should be justified. Since ceramic is formed by reactions between molecular precursors, the homogeneity of the material is perfect at the atomic scale. Moreover, as the starting alkoxides are volatile, their purification is easy and yields materials of high purity. These two major advantages make the sol-gel process extremely interesting for the synthesis of materials for optical purposes.

It is worth citing a few other applications:

1. *Coating*. Thin ceramic films can be produced by dipping substrates into alkoxides solutions. The main application of this process in the formation of coatings.
2. *Controlling properties*. Fibers or materials with controlled porosity can be obtained simply adjusting the viscosity of gels. The porosity of the alcolgel can also allow the migration of ions and the encapsulation of organic molecules.
3. *Synthetic chemistry*. Since the reactions take place at moderate temperatures, it is possible to synthesize and process highly refractory ceramics that could not be obtained by classic melting and casting.
4. *Materials formation*. Since inorganic and organic polymerization are compatible with each other, the use of organo-alkoxides leads to new hybrid materials.

1.3 Heterogeneous catalysis

A powerful tool to enhance the sustainability of chemical processes is undoubtedly catalysis [9].

Furthermore, heterogeneous catalysis allows a few more improvements over the homogeneous one that can contribute to develop cleaner, safer and more economically feasible processes [10].

However, heterogeneous catalysis has to meet numerous requisites in order to be practical:

- the catalyst preparation should be simple, efficient and of general applicability;
- the performance of the immobilized catalyst should be comparable to its homogeneous counterpart;
- the separation of the heterogeneous catalyst from the reaction mixture after reaction should be possible via a simple filtration in which more than the 95% of the catalyst should be recovered;
- the leaching of the active species from the heterogenized catalyst should be minimal;
- the recycling of the catalyst for several cycles should be possible without loss of activity;
- the supports carrying the catalyst should be mechanically, thermally and chemically stable; they should be compatible with the solvent and commercially available in a good quality;
- from an environmental and economical viewpoint, the catalyst selectivity might sometimes become more important than its activity or lifetime.

Usually the heterogeneous catalyst works following these steps (**Figure 1**):

1) Diffusion of reagents on the surface of the catalyst. The diffusion rate depends on density, viscosity and flow of solvent used.
2) Diffusion inside the pores. The fact that reagents should spread within the pores could represent a problem for microporous materials especially in the presence of reagents of a large size.

3) Physical adsorption of the reagents on the surface of the catalyst. This phenomenon originates from Van der Waals forces that are established between the surface and the reagents. The adsorption is weakly exothermic and reversible and it does not derive from the formation of chemical bonds.
4) Chemical reagent adsorption on the surface of the catalyst. Consist in the formation of bonds between the reagent and the surface of the catalyst. This step is more exothermic than the previous one. Formed bonds must be strong enough to prevent premature desorption but not too strong to prevent reactions.
5) Diffusion on the surface. The surface is the physical site where the reagents come into contact one with each other.
6) Reaction. Happens the real product training.
7) Desorption of products. It is a very important step to regenerate the catalyst [11].

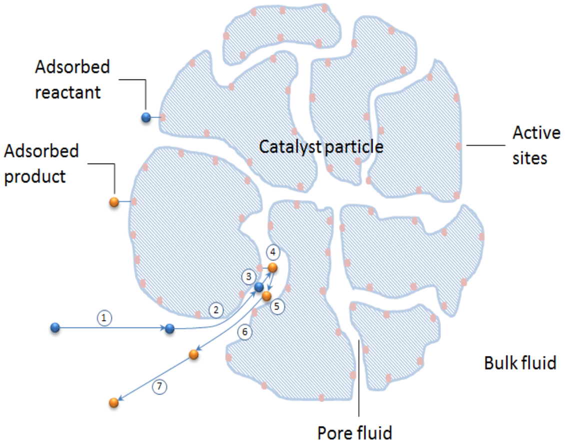


Figure 1.

Kinetically, the reaction rate depends on the frequency of contact of the reactants in the rate-determining step. Usually, the catalyst participates in this slowest step, and rates are limited by the amount of catalyst and its "activity". In heterogeneous catalysis, the diffusion of reagents to the surface and the diffusion of products from the surface are rate determining.

In recent years two preferential tendencies have been developed: polymer-supported catalysts and inorganic oxides heterogenized catalysts [12-13].

In particular the general area of cross-linked polymer supports has shown an explosive growth connected with the development of new macroporous materials that are characterized by a rigid porous matrix that persists even in the dry state [14]. These polymers are typically produced as spherical beads by a suspension polymerization process, which is based on the mixture of cross-linking monomer, inert diluent and the porogen.

Otherwise, it has been reported the preparation of molded porous materials with high characteristics for catalysis and asymmetric catalysis too.

On the other hand, inorganic oxides show several advantages, such as more mechanical stability, easier handling and a wider range of solvents that can be used.

These combine the potential versatility and selectivity of homogeneous catalysts with the practical advantages of solid materials, such as easy catalyst separation from the reaction medium, recovery, and use of a large variety of reaction conditions [15].

However the creation of the ideal supported catalyst is related to the need of new technologies and new supports since they play an important role in the outcome of the process. As a matter of fact, normally, the heterogenization procedure causes a decreasing in stereoselectivity and activity in comparison to the homogeneous counterpart.

Besides, the solid support determines limited diffusion of reactants to the active sites and this results in lower reaction rates. The support surface and the catalyst site surrounding can also influence the extent of the reaction.

The focus of this dissertation regards the immobilization of homogeneous dispersion of perfluorinated sulphonic acid resin, onto solid support for the production of fine chemicals in batch.

1.4 Supported catalysts

In recent years many efforts have been devoted to the catalysts heterogenization and different strategies have been developed for the preparation of supported homogeneous catalysts.

The ideal supported catalyst should thus satisfy many requirements in order to combine both advantages of homogeneous and heterogeneous catalysis [16].

However, the creation of the ideal supported catalyst is far to be accomplished and indeed many problems related to this technology have to be overcome.

First of all the heterogenization procedure usually causes a decreasing in both selectivity and activity of the homogeneous catalyst: as a matter of fact, the solid support causes limited diffusion of reactants to the active sites and this results in lower reaction rates. The lower selectivity too, which often represents a drawback of the heterogeneous systems, has to be ascribed to the matrix effect.

With its chemical and physical properties the support surface in close proximity of the anchored catalytic site can influence the extent of the reaction and determine a lower selectivity.

As an example, when using silica as support, the polar surface can easily form hydrogen bonds with many organic polar functional groups or interact with metal atoms, and this effect can change the spatial orientation of reactants towards catalysts.

On the other hand, organic polymeric supports have usually lower porosity, therefore there is a spatial constriction of catalysts which are not completely free to assume the best orientation.

Moreover, the recyclability of solid catalysts has not yet reached a good level of efficiency to be of practical interest. In this respect there are many problems related to the catalyst and support features. The catalyst can be damaged during the reaction or can undergo partial leaching of the active species in the reaction medium that determines a partial deactivation of the catalyst itself.

In some cases, however, the supporting procedure can improve the catalyst stability by eliminating, dimerization, and/or aggregation effects, which are the main causes of deactivation under homogeneous conditions. As a matter of fact "site isolation", i.e. attaching the catalyst to a support in such a way that the active sites can no longer interact with each other, is a key concept that might lead to better performing heterogeneous catalysts [17].

With a careful catalyst design and an appropriate support choice based on reaction conditions (e.g. solvent, temperature, reactant etc.) it could be possible to overcome these drawbacks.

1.4.1 The anchoring methodologies

Concerning the catalyst heterogenization, there are almost three approaches that have been described in the literature [18] (**Figure 2**): a) formation of covalent bonds; b) adsorption by ion pair formation; c) entrapment.

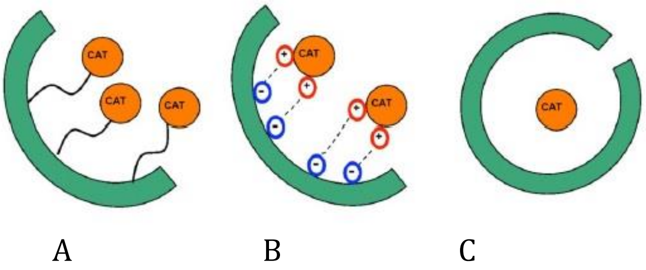


Figure 2. Anchoring methodologies: A) covalent binding; B) adsorption; C) entrapment

Covalent binding

Covalent binding, by far the most frequently used strategy, can be made either by copolymerization of conveniently functionalized catalysts or ligand with a suitable monomer, or by anchoring catalysts or ligands with reactive groups to a performed surface [19]. With both strategies it is possible to prepare whole organic materials (polymeric materials) and organic-inorganic materials (mixed gels and organic molecules tethered on inorganic supports) [20- 21].

Several specific methodologies usually employed to covalently anchor to solid supports will be fully described in the following chapters.

The heterogeneous catalysts are much more complex than their homogeneous counterparts, and many additional parameters such as type of support, spacer length and flexibility, surface coverage degree, surface area and porosity have to be optimized to achieve an acceptable catalytic performance.

Heterogenization via adsorption and ion pair formation

This approach relies on various absorptive interactions between the carrier and the catalyst (usually a metal complex) [22-23].

In general this strategy suffers from limitations connected to the leaching of the active species in the solution phase. The leaching makes problematic the recycling of the catalyst and the purification of the product from the released catalyst.

Heterogenization via entrapment

In this case, the size of the catalyst is more important than a specific adsorptive interaction. There are two different preparation strategies [24, 25].

The first strategy, often called “ship in the bottle” approach, is based on building up catalysts in well-defined cages of porous supports. The other approach consists on creating up an inorganic sol-gel or organic polymeric network around a preformed catalyst. However, entrapped catalysts were much less active than their homogeneous counterparts.

1.4.2 Solid supports

The development of supported catalysts for heterogeneous reactions prompted research groups all over the world to investigate many different solid supports as these play an important role in the outcome of the process. Solid supports can be roughly divided in two classes: inorganic materials and organic polymers.

Inorganic materials

Many different types of inorganic supports are known for the preparation of heterogenized catalysts. The most used can be divided in three big categories: a) amorphous materials (e.g. amorphous silica and alumina), b) mesoporous materials (e.g. MCM-41, MCM-48 and MSU silicas) and c) crystalline materials (e.g. zeolites).

Amorphous silica

Amorphous silica has a non-ordered structure with irregular channels and pore diameter that can broadly vary. These materials have the advantage to be readily available and economically advantageous. However, due to the irregular pore sizes, part of the catalyst can penetrate into small pores during the supporting procedure with the consequence that this part of the catalyst is not easily accessible from reactants.

Mesoporous synthetic silicas (MCM-41)

Ordered mesoporous (alumino)silicates offer interesting catalytic properties. These materials are synthesized with the help of surfactant micelle templates. Exemplified by the Mobil M41S materials, of which MCM-41[26-27] is the most familiar, they possess uniform channels with tunable diameters in the range 1.5-10 nm.

M41S family is composed by three types of materials which have a very high surface area (often more than 700 m^2/g) and which differ for the mesoporous spatial organization:

- MCM-41 with a mono-dimensional array of hexagonal channels
- MCM-48 with three-dimensional network of cubic channels
- MCM-50 with lamellar, but not very stable, organization of channels.

MCM-41 is the most studied and employed material of the M41S family. The practical advantage in using MCM-41 as support for catalyst immobilization lies in its high surface area and pore volume. Thus reactant and product molecules can easily diffuse and reach the catalytic sites, bulk catalysts can be accommodates in the mesopores (usually falling in the range 3-6 nm depending upon the synthesis conditions) and well-isolated and non-interacting catalytic site can be obtained. The typical XRD pattern of MCM-41 shows an intense peak at low diffraction angles (reflection line) and three less intense peaks at higher diffraction angles. This type of diffraction pattern is typical of a hexagonal symmetry distribution of regular sized cylindrical mesopores.

MCM-41 is usually defined as a long-range ordered structure because the material at the atomic level is amorphous and does not present a short-range organization (as for example zeolite aluminosilicates).

Organic Polymers

Organic polymers as solid phases for heterogeneous catalysis [28-29] are mainly of three types: soluble polymers (linear no cross-linked), cross-linked insoluble polymers and macroreticulated resins.

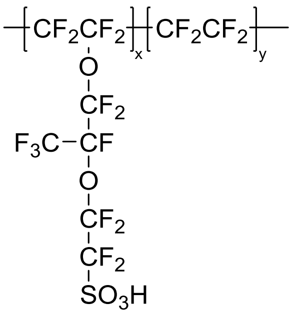
1.5 PFSA

The sulphonic group showed to be a very active acid catalyst. Recent interests aimed at developing methods of eco-friendly synthesis have led to the abandonment of mineral acids such as sulphuric acid, hydrochloric acid and hydrofluoric acid.

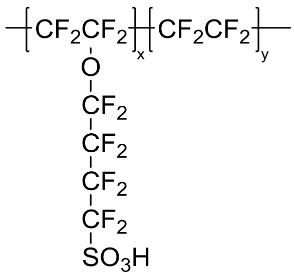
Perfluorosulphonic resins present in the main chain branching the sulphonic groups. They were mainly used in the development of supported sulphonic catalysts.

This class of molecules are commonly called PFSA (PerFluoro Sulphonic Acid).

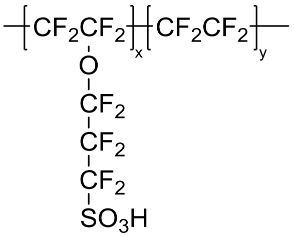
Several resins such as Nafion, 3M, Ashai and lastly Aquivion are nowadays available on the market today.



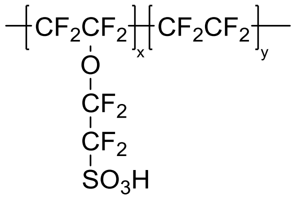
Nafion



3M



Ashai



Aquivion

Nafion born as exchangeable membrane [30] used in fuel cells. Its catalytic activity as acid catalyst is well established in various reactions such as alkylation, acylations, isomerizations, esterification and etherification [31].

It was also used as metal support for Rh, Ru, Pt for example in various reactions such as hydroformylation, hydrogenation and oxidation [32].

All these resins are semicrystalline polymers: the part of tetrafluoroethylene chain segments is crystalline while the sulphonic vinyl ether pendant constitutes the amorphous part.

Aquivion, recently introduced on market, is the PFSA ionomer with the lower aliphatic chain, used as membrane exchanger in fuel cell.

It is similar to Nafion but has some fundamental differences that improve its performance. The acidity of Nafion and Aquivion is about the same (H_0 = -12), but Aquivion has a higher loading of the acid sites per kg of powder (0.8 mol SO_3H/kg of Nafion powder against 1.5 mol SO_3H/kg of Aquivion powder).

In addition, it has a glass transition temperature of 140 °C, higher than Nafion that has a T_g of about 100 °C and 3M has a T_g of 125 °C (**Figure 3**).

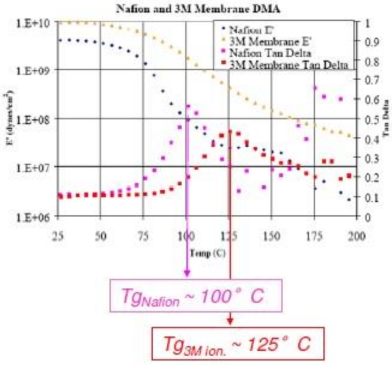


Figure 3.

Then, Aquivion has the T_g 40 % higher than that of Nafion. This allows the use of Aquivion at higher temperature.

Thanks to its shorter chain, Aquivion has better mechanical properties than long chain ionomers with the same content of sulphonic groups. The resin tends to crystallize and "see" the side chain as impurity: more this chain is short, more increases the degree of crystallinity (**Figure 4**).

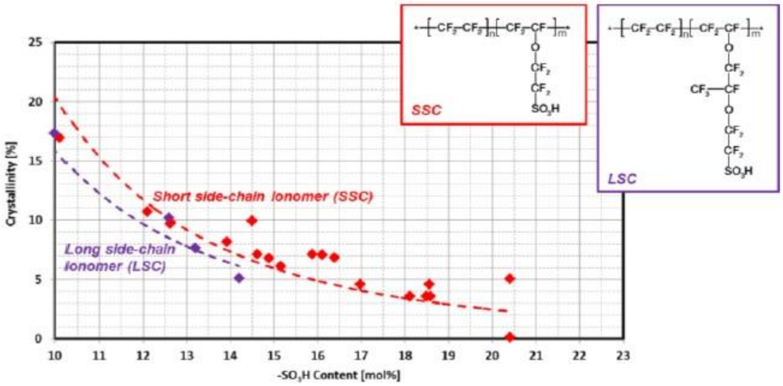


Figure 4.

Its properties guarantee less solvent swelling, increased friction resistance, and lower leaching if immobilized on silica and other inorganic support, because if the polymer is completely amorphous it swells too much and tends to be drained from the support.

1.6 Oxidation reactions in Green Chemistry

Oxidation reactions are characterizes by the loss of one or more electrons by a chemistry species. They are widely used as chemical transformation but they have as important limitations the production of high amount of wastes and the employment of hazardous oxidants.

Historically, oxidation reactions were conducted with inorganic oxidants compounds such as Cr(VI) and Mn(VII) salts in stoichiometric amount, which have as major drawbacks the generation of toxic wastes and the high cost [33-34]. Industrially nitric acid is the most used oxidant because of its easier availability, but it generates numerous oxides as by-products.

In recent years, studies focused on the development of green methods allow the use of non-hazardous, inexpensive and easy-to-handle oxidizing agents such as hydrogen peroxide and molecular oxygen [35-36].

It is possible to identify four typologies of ecofriendly oxidations:

1) steam phase with molecular oxygen in heterogeneous catalysis;
2) liquid phase with molecular oxygen and homogeneous catalysis;
3) liquid phase with hydrogen peroxide and homogeneous catalysis;
4) liquid phase with heterogeneous catalyst and hydrogen peroxide or hydroperoxides.

The hydrogen peroxide is a very good oxidizing agent and it responds perfectly to eco-compatibility, since nowadays its production is eco-compatible [37] and due to the fact that its only by-product is water. Thanks to its peculiarities it is the subject of many studies aimed at its use. Unfortunately, hydrogen peroxide requires high activation energy to effectively act as oxidant and therefore it needs to be accompanied by a suitable catalyst. In literature some oxidation reactions with hydrogen peroxide using supported sulphonic acids as catalysts are already known: for example oxidation of benzoquinone to hydroquinone [38] and sulphide oxidation [39].

Molecular oxygen is also an excellent oxidizing agent, more beneficial in terms of atom economy compared to hydrogen peroxide and also in this case were conducted several studies using oxygen as oxidant, but with the use of different metals as catalysts [40-41].

Recently oxidation reactions of hydrocarbons with O_2 using metalloporphyrins as catalyst were studied [42].

In this thesis work, a more innovative and less explored road of oxidation reaction was studied, using supported metal free polymers as organic catalysts such as perfluorinated sulphonic acid resins (PFSA).

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2 Silica supported acid catalysts

2.1 Heterogeneous acid catalysis

Brönsted and Lewis acids are the most important and common catalysts [1]. Many organic reactions such as aldol condensations, nucleophilic additions, hydrolysis, acylations, etc. are catalyzed by these acids. However, the use of soluble acids or corrosive mineral acids such as HF, HCl, CH_3COOH, HBr, CF_3COOH and H_2SO_4 is associated with a great number of environmental and economic problems. Indeed, huge amounts of catalyst are needed, and troublesome work-up steps are also required when Lewis acids are employed. Moreover, an excess of these acids is in most cases required, and a huge quantity of anions (especially chloride) is released in aqueous media [2]. The recovery of the catalyst from the reaction mixture is very difficult and some related problems should be taken into account, such as the need of neutralization, the impossibility of the catalyst reuse and the reactor corrosion. The use of a solid acid that can be separated by filtration and reused could represent a major breakthrough [3].

Hence, recyclable acid catalysts such as solid acid zeolite [4], solid super acid sulphated zirconia [5], silica sulphuric acid [6], alumina sulphuric acid [7], tungstate sulphuric acid [8], molybdate sulphuric acid [9], $ZrOCl_2{\cdot}8H_2O$ [10],MCM-41-SO_3H [11], PPA-SiO_2 [12], SiO_2-$HClO_4$ [13], SiO_2-$NaHSO_4$ [14], SiO_2-Pr-SO_3H [15], Amberlyst [16], heteropoly acids [17] and montmorillonite K-10 [18] were employed in the synthesis of wide range of organic compounds. These solid acids have a lot of advantages over conventional acid catalysts such as ease of handling, mildness, cost-effective, selectivity and decreased reactor and plant corrosion problems. However the biodegradability and lower reactivity of these heterogeneous catalysts are still the major problem for organic synthesis.

Zeolites in their protonated form are the most widely used solid acids in petrochemistry [19] and gas phase reactions. Zeolites working in gas-phase and continuous flow processes are the typical examples of non-toxic, reusable, highly selective solid catalysts. However, when moving from the scale of petrochemistry to fine chemistry and liquid phase reactions, zeolites could not be suitable for all reactions.

The small pore size available (< 1.0 nm even for the so called large pore zeolites) that imposes a severe restriction for the accessibility of larger molecules to the internal surface of the catalyst, is probably the main drawback of zeolites.

In order to overcome the problem of the pore size, the synthesis of mesoporous materials by Mobil researchers constituted a breakthrough due to the possibility of opening the catalysis by solid acids to the large molecules typical of fine chemistry [20]. The most widely used mesoporous silica is known as MCM-41. However, it was realized soon that the use of mesoporous silicas and aluminosilicates as solid acids could not meet the initial expectations, mainly because of the low acid strength of their acid sites. An alternative to the use of the mild acid sites in their aluminosilicates framework is to employ these mesoporous silicas as supports to covalently anchor strong acid sites.

The functionalization of mesoporous silica with organic compounds began with the surface modification using silane compounds such as $R\text{-}Si(OR')_3$ [21-23]. After this kind of approach, the framework modification using disilane compounds followed. These materials are commonly called periodic mesoporous organosilicas (PMOs) [24-26]. For example, Inagaki and co-workers notified that benzene ring and analogues are completely incorporated into the framework of mesoporous silica materials; moreover these materials are effective acid catalysts after sulphonation [27]. It is important to remember that sulphonic acids are organic compounds that exhibit an acid strength comparable to those of sulphuric and benzenesulphonic acids, strong acids frequently used in organic solvents [28]. Subsequently, other research groups have introduced variations in the preparation of MCM-41-SO_3H materials [29-31]. These improvements have focused on the synthesis of MCM-41-SO_3H in a single step, the optimization of the mercapto/sulphonic oxidation step, the control of the MCM-41 pore size, the protection of the residual silanol groups, etc. [32-33].

With respect, for example, to polymeric arenesulphonic acids, the obvious advantage of MCM-41-SO_3H, and also of amorphous silica, is the large surface area of these materials (> 250 m^2/g) compared to cross-linked polystyrene (~ 50 m^2/g), this factor results in a higher catalytic activity as a consequence of the easier accessibility of substrates to the acid sites [34].

Another trend is the polymerizations in the pore voids of mesoporous materials: many researchers produced composite materials with the corresponding polymers by this method [35]. Mesoporous composite materials, where an organic polymer is introduced into their framework, were also investigated. In 2000, Fujiwara and co-workers, reported that Nafion resin, was incorporated in the framework of M41S type of mesoporous silica [36].

This material proven to be a good catalyst for α-methylstyrene dimerization. In **Figure 1** is proposed a classification of these composite materials of mesoporous silica with organic components.

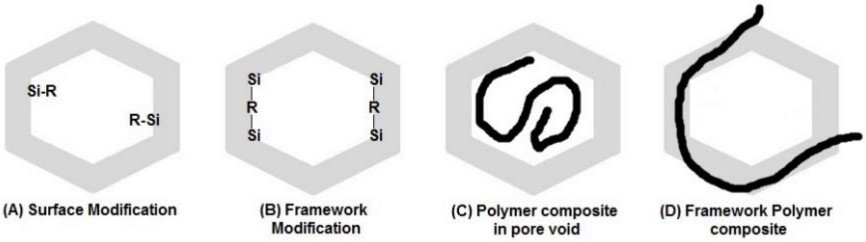

Figure 1. Conceptual schemes of composite materials of mesoporous silica with organic components

Type (A) is surface modification using R-Si(OR')$_3$ compounds, and Type (B) is framework modification such as periodic mesoporous organosilicas (PMOs). Type (C) shows composite materials with polymeric compounds in the pore voids. Composite mesoporous materials with polymers in the framework are named Type (D).

2.2 Materials and methods

All the reagents were used as received without further purifications. The mesoporous siliceous support (MS-SiO_2) was dried at 100 °C for 5 hours, before functionalization. MS-SiO_2 mesoporous silica was prepared, according to the procedure reported in literature [37], by mixing, 2 g of polyacrylic acid (MW = 25000), HCl, 31 mmol of cetyltrimethylammonium bromide (C_{16}TAB), 90 mmol of tetraethoxysilicate (TEOS), NH_3 solution and water, at room temperature and under vigorous stirring. The solution was kept under stirring for 24 hours at room temperature, then filtered, dried at 90 °C in a oven and subsequently calcined at 600 °C for 6 hours.

Catalysts -(C_6H_4)-$SO_3H@SiO_2$, -(CH_2)$_3$-$SO_3H@SiO_2$ and -(CF_2)$_3$-$SO_3H@SiO_2$, were prepared according to literature [38]. N_2 adsorption-desorption isotherms, were used to determine specific surface areas, the pores volume and their dimension were obtained at 77 K on an ASAP 2020 apparatus of Micromeritics. Before each measurement the samples were outgassed at 383 K for 1 hour.

The surface acidity was determined by a reported titration method [39].

The ATR-FT-IR spectra were acquired through the instrument Nicolet 5700 FT-IR on diamond.

TEM analysis were performed with a microscope FEI CM12.

The samples were dispersed in isopropyl alcohol and a few drops of these suspensions were deposited on carbon coated grids with a film of Cu.

2.3 Catalysts synthesis

The following materials were prepared using Sol-Gel methodology.
The addition of Aquivion, which carries the sulphonic acid sites, has been made directly during the synthesis of the inorganic support, or through impregnation of the mesoporous support previously prepared.
Three silica-Aquivion based materials were prepared:

- Aquivion@AM-SiO_2
- Aquivion@MS-SiO_2
- Aquivion@NP-SiO_2

In all three cases the Aquivion was added at 10% by weight respect the support.

Aquivion@AM-SiO_2:

2.5 g of Aquivion dispersion D66-20BS at 20.1 % were added to a solution of NaOH (43 mmol) and surfactant (cetyltrimethylammonium chloride 25 % solution, 10 mmol). The mixture was stirred for at least 1h to dissolve all the surfactant. Then TEOS (80 mmol) was added dropwise with a funnel drop.
The final solution was stirred at room temperature for 16h.
The solid was filtered through Büchner funnel, washed with H_2O and dried in an oven at 80 °C for 12h.
The obtained powder was placed under reflux with a 1M solution of H_2SO_4 in EtOH (1 g of powder/150 ml of solution) for 12h to remove the surfactant and to reactivate acid sites.
The solid was filtered again and it was placed under reflux with only EtOH for 12h. Finally, the powder was filtered again, washed with H_2O and dried at 80 °C for 12 hours.

Aquivion@MS-SiO_2:

In a round bottom flask 2.5 g of ground mesoporous support, previously prepared [37], were suspended in 50 ml of distilled water within an ultrasonic bath for 30 minutes.

The homogeneous mixture thus obtained was transferred in an open glass vessel and 1.25 g of Aquivion dispersion D66-20BS was added under stirring at room temperature.

This dispersion was heated under stirring at 80 °C for 6 hours and then cooled down (always under stirring) overnight.

The white opaque and viscous gel obtained was heated in a vent oven at 80 °C for 5 hours and then at 150 °C overnight.

The off-white powder was recovered and eventually ground into a manual mill.

Aquivion@NP-SiO_2:

2.5 g of Aquivion dispersion D66-20BS at 20.1 % were added to a solution of NaOH (43 mmol) and surfactant (dimethydioctadecylammonium bromide, 5 mmol). The mixture was stirred for at least 1h to dissolve all the surfactant. TEOS (80 mmol) was then added dropwise with the aid of a funnel drop. The final solution was stirred at room temperature for 16h.

The solution is then transferred into a crystallizer and left gelating and age for a few days, then put it in an oven to dry at 100 °C overnight.

The obtained powder was placed under reflux with a 1M solution of H_2SO_4 in EtOH (1 g of powder/200 ml of solution) for 12h to remove the surfactant and to reactivate acid sites.

The solid was filtered again and it was placed under reflux with only EtOH for 12h.

Finally, the powder was filtered again, washed with H_2O and dried at 100 °C for 12 hours.

2.4 Catalyst characterizations

2.4.1 Infrared analysis

IR spectra were performed on the Aquivion powder, on the Aquivion dispersion used in the synthesis of catalysts and finally on all prepared catalysts.

In the Aquivion powder spectrum (**Figure 2**), the band around 1700 cm^{-1} can be attributed to the asymmetric bending of the H_3O^+ species and the free H_2O bending due to the adsorbed moisture on the organic resin.

The peak at 1200 cm^{-1} is related to the stretching of the -CF_2 and -CF groups, the very intense peak at 1160 cm^{-1} and the less intense one at 1030 cm^{-1} are due respectively to the stretching of the -S-O single bond and double bonds O=S=O of the -SO_3H groups and finally the peak at 970 cm^{-1} results from the stretching of side chain bond C-O-C.

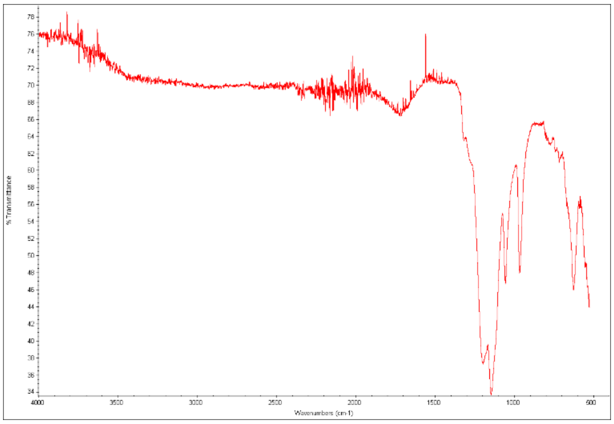

Figure 2. Aquivion PW66S powder FT-IR spectrum

The aqueous Aquivion dispersion spectrum (**Figure 3**) shows the same peaks, of lower intensity, found in polymer powder, and of course the 3400 cm^{-1} band water stretching and the water and H_3O^+ ion bending peaks more intense.

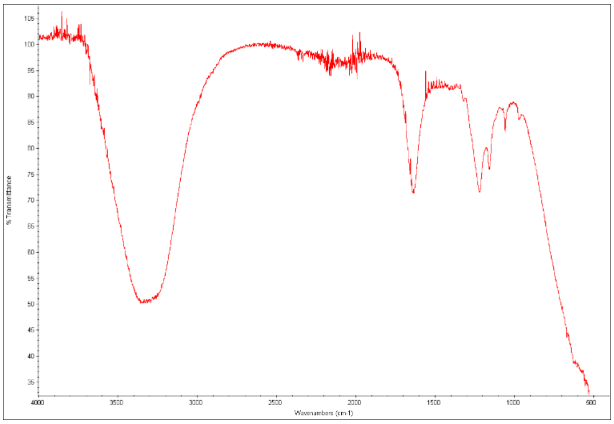

Figure 3. Aquivion D66-20BS dispersion FT-IR spectrum

All the spectra of catalysts (**Figure 4-6**), on the other hand, are very similar one to each other and have the same characteristic peaks: the band of different intensity at 3419 cm^{-1}, relative at -OH bonds of water retained that form hydrogen bonds, the very intense peak around 1030 cm^{-1} attributable to the stretching of the Si-O-Si bonds, and finally the less intense peaks at about 900 and 800 cm^{-1}, which are related, respectively, to the stretching and bending of the -SiOH present on the silica surface.

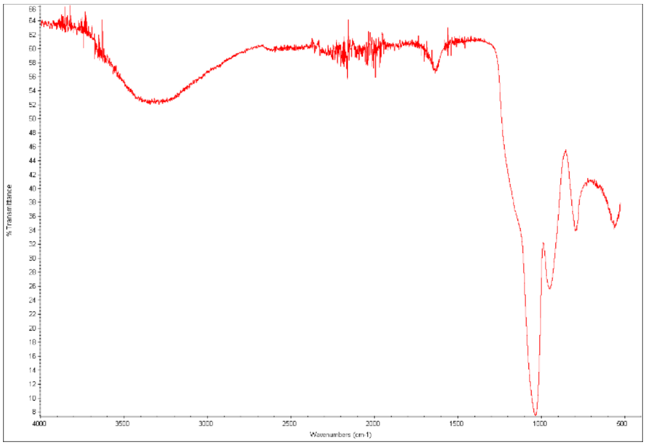

Figure 4. Aquivion@AM-SiO_2

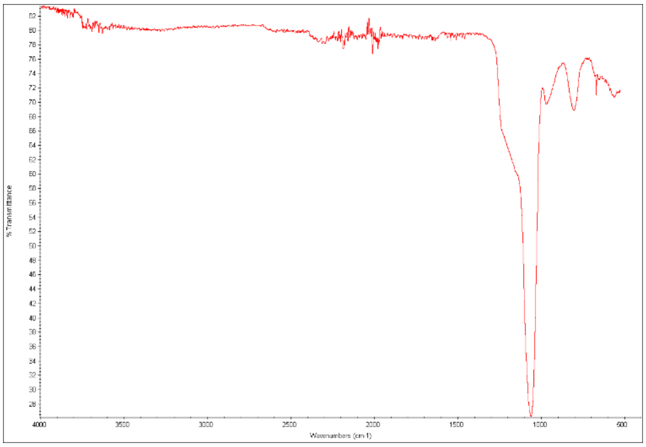

Figure 5. Aquivion@MS-SiO_2

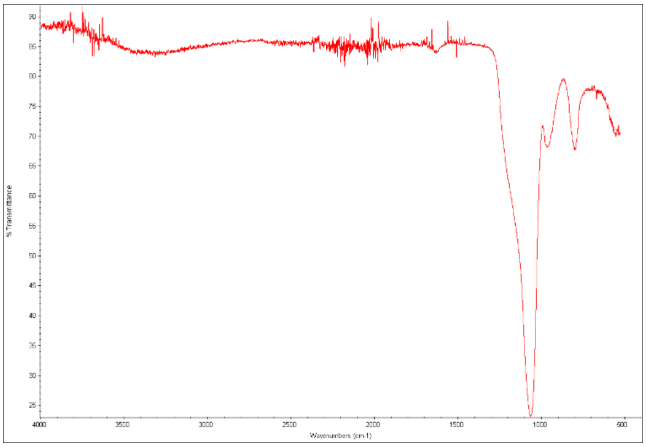

Figure 6. Aquivion@NP-SiO_2

Unfortunately IR spectrometry cannot be considered a diagnostic technique to quantify the amount of Aquivion loaded on the surface of the catalyst, since its characteristic peaks and silica stretching bands overlap.

2.4.2 Surface properties

Nitrogen adsorption-desorption measurements were performed at liquid nitrogen temperature (-196 °C) with an ASAP 2020 instruments of Micromeritics. Before each measurement, the samples (0.1 g) were degassed first at 110 °C for 1 hour at $5 \cdot 10^{-3}$ Torr and then at room temperature for 1 hour at $0.75 \cdot 10^{-6}$ Torr. The N_2 isotherms were used to determine the specific surface areas and the pores volume and their dimension through the BET equation ($S.A._{BET}$). Results are reported in **Table 1**.

The specific pore volume (Vs) was calculated at p/pº = 0.98, and pore size distributions were calculated from the BJH [40] method, calculated from the adsorption branch.

Table 1. Surface area and surface property of tested catalysts

Catalyst	$S.A._{BET}$ (m^2/g)[a]	V_S (cm^3/g)[b]	D_P (nm)[c]	D_N (nm)[d]
Aquivion@AM-SiO_2	626	0.16	2.1	9.6
Aquivion@MS-SiO_2	827	2	7.8	7.3
Aquivion@NP-SiO_2	224	0.8	14	27

[a] specific BET surface area; [b] specific pore volume at p/pº; [c] diameter of pores according to the maximum of the BJH pore size distribution; [d] nanoparticle size.

The N_2 adsorption-desorption isotherms of the functionalized silica materials are shown in **Figure 7**.

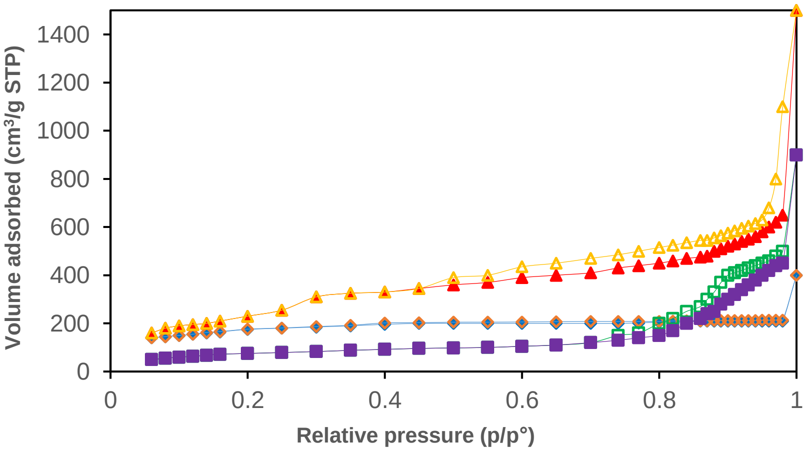

Figure 7. N_2 adsorption (full symbol) – desorption (empty symbol) isotherms of the materials Aquivion@AM-SiO_2 (♦), Aquivion@MS-SiO_2 (▲) and Aquivion@NP-SiO_2 (■)

The isotherms of Aquivion@AM-SiO_2 material is classified as Type I, according to that of microporous materials [40]. Pore size distribution of this sample, estimated employing the BJH method, indicates that microporosity of the material is not well ordered.

The Aquivion@MS-SiO_2 material exhibits a reversible Type IV isotherm with a H1 hysteresis loop, typical of mesoporous adsorbents. The pore size distribution is very sharp and centered at 7.8 nm. The total pore volume V_s of this material calculated from the N_2 amount adsorbed at p/p° close to saturation vapor pressure (p/p° = 0.98) is almost the same value, about 2 cm^3/g.

Also the Aquivion@NP-SiO_2 material presents a Type IV isotherm, but in this case the pore size distribution is more widespread, centered at about 14 nm.

The surface acidity was determined by a reported titration method [39]: 0.5 g of the catalyst sample was added to 50 ml of NaCl solution (200 mg/L) and stirred at room temperature. The ion exchange between H^+ and Na^+ was allowed to proceed for 24 hours. The catalyst was filtered off and washed with distilled water, then the mixture was titrated with 0.01 M NaOH solution using phenolphthalein as pH indicator. Results are reported in **Table 2**.

Table 2. Surface acidity of tested catalysts

Catalyst	**Surface acidity (mmol H^+/g)**
Aquivion dispersionD66-20BS	2.18
Aquivion powder PW66S	1.37
Aquivion@AM-SiO_2	0.03
Aquivion@MS-SiO_2	0.31
Aquivion@NP-SiO_2	0.27

2.4.3 Transmission electron microscopy analysis

TEM analysis, were performed on the synthesized material to verify their really structure and try to understand the interaction between Aquivion polymer and the support surface.

The **Figure 8a-b** shown the results of TEM analysis of Aquivion@AM-SiO_2 material.

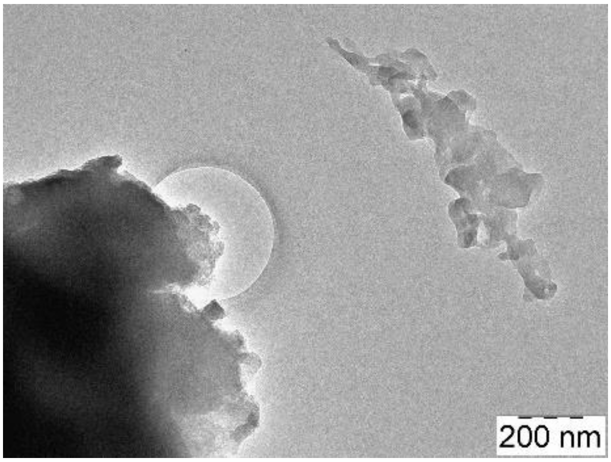

Figure 8a.

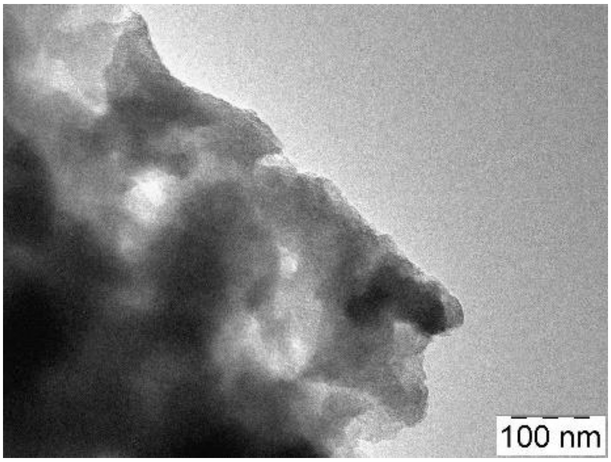

Figure 8b.

The **Figure 8a-b** depict silica agglomeration with a detached part that could be attributed to free ionomer. The EDX analysis indicated the presence of silica for the left agglomeration, formed by particles of 10-50 nm of diameter. **Figure 9** depicts the enlargement of the supposed the ionomeric particle. In this case the EDX analysis was unable to detect the composition because of the side scattering, but the signal of the Si was lower, and the signal of Fluorine appeared. An ionomer micelle was about 20-50 nm.

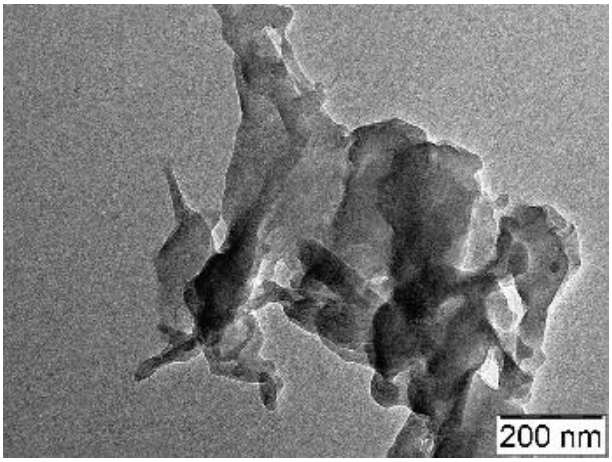

Figure 9.

Figure 10 shown the TEM image of Aquivion@MS-SiO_2 catalyst. The mesoporous structure of the material was clearly visible. In some areas was can clearly see the silica channels. In other areas, the structure seem more amorphous, probably due to the presence of adsorbed organic polymer. There were also traces of non-adsorbed resin.

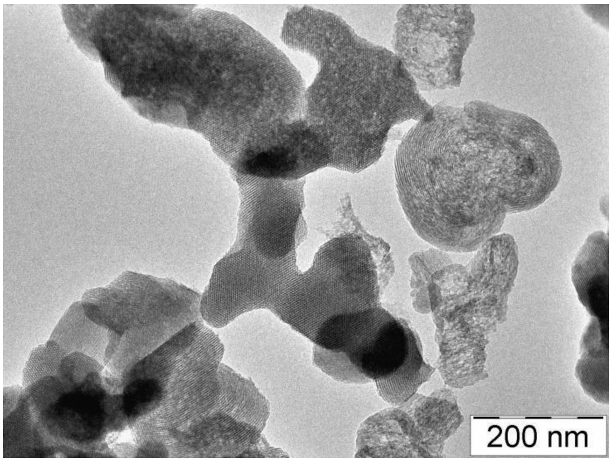

Figure 10.

Figure 11a-b compared the different areas of Aquivion@MS-SiO_2 material. **Figure 11a** shows an irregular areas where the resin was present. Otherwise in the **Figure 11b**, the particles are regular and the crystalline, polymer-free structure are clearly visible. Areas free of organic material are crisp and the particles have a regular arrangement of their crystallographic planes.

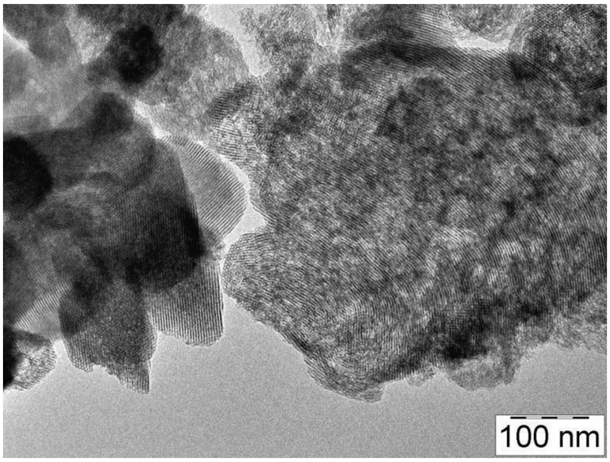

Figure 11a.

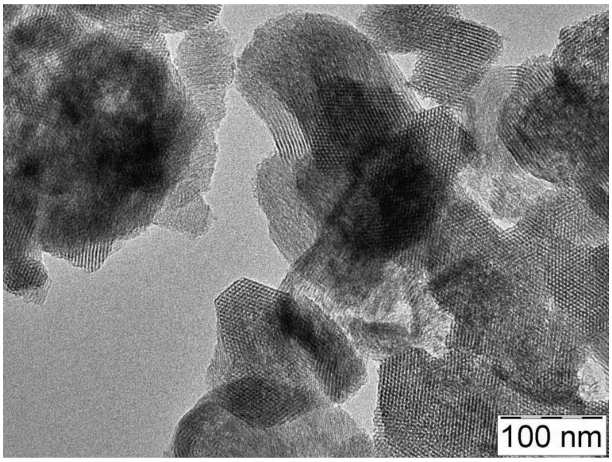

Figure 11b.

TEM analysis on the Aquivion@NP-SiO_2 catalyst (**Figure 12a-b**) shown surprisingly that the hybrid material is formed by agglomerates of silica nanoparticles evenly decorated by the perfluorinated polymeric resin.

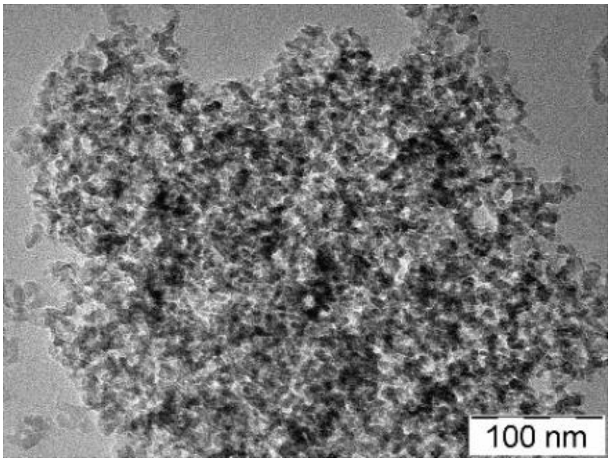

Figure 12a.

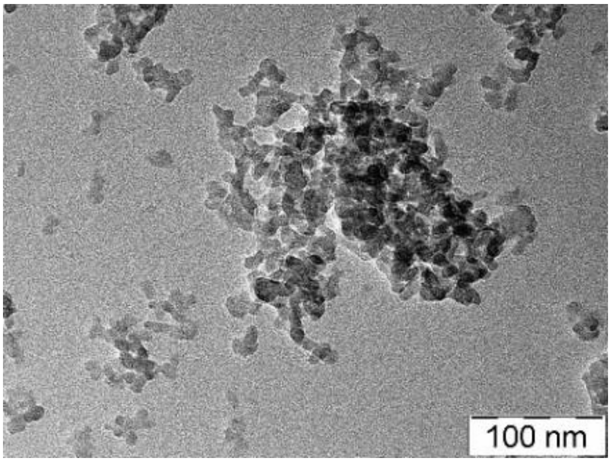

Figure 12b.

This finding suggest that the Sol-Gel preparation in the presence of the perfluorosulphonate ionomer inhibited the formation of a mesoporous inorganic scaffold while favoring agglomeration on nanoparticles. However, thanks to the ammonium template however, nucleation of silica proceeded in a controlled fashion. This delivered a narrow dispersion of the nanoparticles themselves (3-7 nm, **Figure 13a-b**).

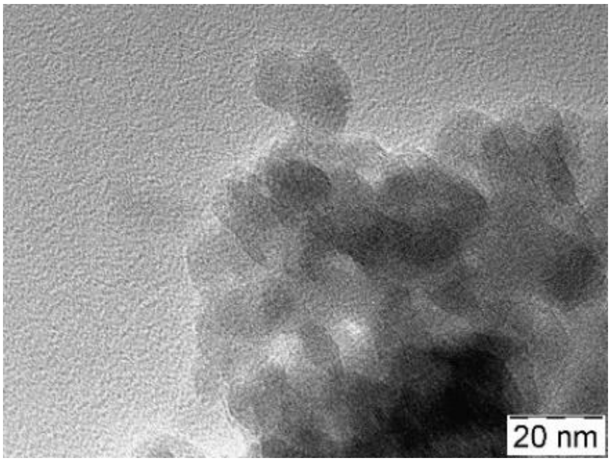

Figure 13a.

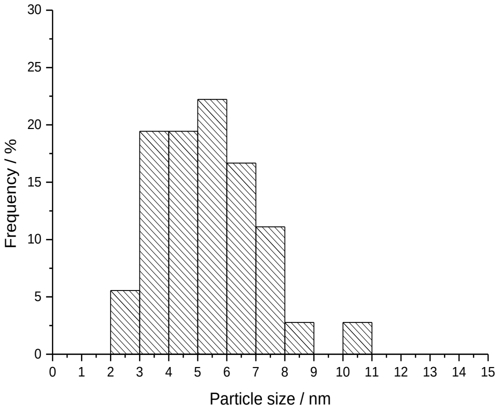

Figure 13b.

EDX analysis on the material further confirmed that the inorganic and the organic phases are evenly dispersed.

The method thus enables the preparation of perfluorosulphonate ionomer-coated narrowly-dispersed silica nanoparticles.

2.5 References

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3 Supported polymeric sulphonic acids as novel catalysts for selective oxidation of benzylic methylenes to carbonyls

3.1 Introduction

Nowhere there is a great need for green catalytic options in fine chemical manufactures obtained by oxidation reactions. In contrast to reductions, oxidations are still largely carried out with stoichiometric inorganic or organic oxidants such as chromium(VI) reagents, potassium permanganate, manganese dioxide, periodates or benzoyl peroxide, meta-chloroperoxybenzoic acid, peracetic acid and *tert*-butyl hydroperoxide.

Thus catalytic alternatives employing clean primary oxidants such as oxygen or hydrogen peroxide are strongly needed.

Catalytic oxidation with O_2 is widely used in the manufacture of bulk petrochemicals [1], but application to fine chemicals is generally more difficult, due to the multifunctional nature of the target molecules. However, in some cases such technologies have been successfully applied. An elegant example is the BASF process [2] for the synthesis of citral, a key intermediate for fragrances and vitamins A and E. The key step is a catalytic vapor phase oxidation over a supported silver catalyst, basically the same as that used for the synthesis of formaldehyde from methanol.

Many other different oxidation reactions are of great interest at both academic and industrial level, such as epoxidation of alkanes, Bayer-Villiger oxidation of ketones, oxidation of alcohols to aldehydes, sulphoxidation, etc. As noted above, in all these cases there is an urgent call for greener methodologies, preferably employing O_2 or H_2O_2 as clean oxidants and effective with a broad range of substrates.

Hydrogen peroxide is an ideal oxidant for many reason, mainly due to the fact that it is cheap, and water is theoretically the only by-product [3-5]. The activation of aqueous hydrogen peroxide is a challenge that has attracted many research groups in order to perform oxidation reactions, under environmentally friendly conditions [6-7].

From a mechanistic point of view, the activation of hydrogen peroxide can take place in three ways [8]. First, in the presence of metal catalysts, according to the well-known Haber-Weiss reaction, involving the hydroxyl radical, that frequently leads to unselective processes in organic synthesis [9]; second, in the presence of a base, through the formation of the strong HOO^- nucleophile, that can oxidize, for example, electrophilic alkenes [3]; third, according to the heterolytic oxidation process, that is probably the most important reaction from a synthetic point of view [10].

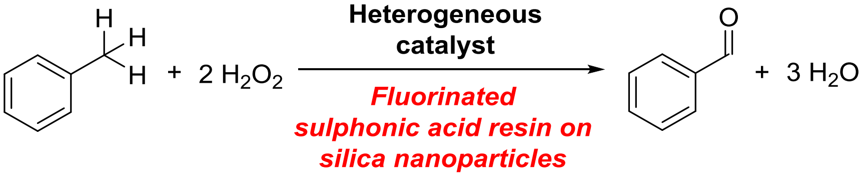
In the presence of catalysts containing different transition metals such as Ti, W, Mn, Re and Sn [11-15], hydrogen peroxide promotes efficient oxidation reactions, for example alkene epoxidation [16-19], conversion of sulphides into sulphoxides and sulphones [20-23] and Bayer-Villiger oxidation of ketones to lactones [24-27]. In all these cases the reaction involves an electrophilic activation of hydrogen peroxide; the same mechanism is reported with fluorinated solvents, as it was clearly shown by Sheldon and Berkessel [28-29].

With regard to the crucial role of peracids added to the reaction mixture or produced in situ from carboxylic acids, many studies are reported in the literature [30]; however the role of different acids such as sulphonic, arsenic and phosphoric acids showing a similar behavior is not as much studied and needs further deepening. For example, resin supported-sulphonic acids were reported to be good heterogeneous and reusable catalysts for the Bayer-Villiger oxidation of cyclopentanone [31-32], and more recently Sato reported a very efficient procedure for the solvent-free dihydroxylation of alkenes with hydrogen peroxide in the presence of Nafion resin [33].

Another important methodology among oxidation reactions, especially when considering industrial applications, is the direct C-H oxidation. In particular, benzylic oxidation is one of the most useful tools to generate valuable building blocks that can serve to access many drugs, agrochemicals and various natural products [34]. Numerous C-H oxidation methods have been therefore developed to date [35]. Toluene is the prototypical aromatic hydrocarbon that possesses C-H benzylic bonds. It can be oxidized to several oxygenates, namely benzyl alcohol, benzaldehyde and benzoic acid, which are all useful chemical intermediates. Among these, benzaldehyde is the most desirable product, both for its immense importance in our daily life [36] and for the intrinsic chemical challenge to hamper its overoxidation.

In the past, benzaldehyde was usually produced in a multistep process starting from toluene chlorination [37], nowadays in the Rhodia, Dow and Snia-Viscosa processes liquid phase oxidation of toluene is carried out over homogeneous metal salt catalysts using oxygen or peroxides as oxidants in industrial grade [38]. The sustainability of the process suffers from the amount of generated wastes. There are several elegant reports on the oxidation of toluene to benzaldehyde. This is achieved using a metal-based catalyst and H_2O_2 or molecular O_2, which are clean oxidants, although at the expense of either yield or selectivity [39-41]. On the other, such limitations can be efficiently countered by using proper catalysts in combination with molar excesses of hypervalent iodine reagents or organic peroxides [42-43], which ultimately affect however the environmental cost of the whole process. Most of these methods require the use of transition-metal catalysts too.

Herein we report a simple and practical double benzylic sp^3 C-H oxidation in the presence of hydrogen peroxide using supported solid sulphonic acid catalyst.



3.2 Results and discussion

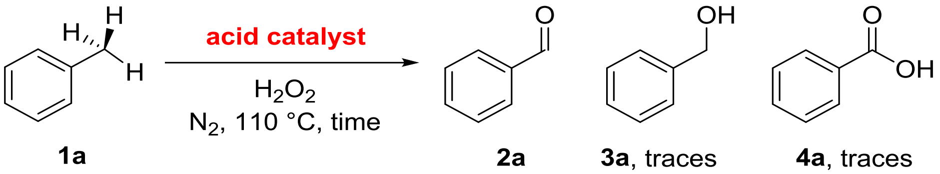
Our investigation began while we were screening proper conditions for Friedel-Crafts acylations. We observed unexpectedly the formation of traces of benzaldehyde **2a** employing non-degassed solutions in combinations with strong Brönsted acid catalysts.

Warming an aerated toluene solution in the presence of Amberlyst IRA-400 at 110 °C for 24 hours delivered 1% of **2a**.

Under these conditions, toluene oxidation remained largely unpractical, but intrigued by this responsiveness we decide to optimize the reaction. We investigated various catalysts and conditions, replacing air with hydrogen peroxide as oxidant.

In a typical experiment, 5-10 mmol of freshly degassed toluene are warmed at 110 °C with 30% aqueous solution of H_2O_2 in the presence of 100-200 mg of solid acid under nitrogen for 24 hours. Upon cooling, the solid is filtered and the resulting biphasic mixture separated. The organic phase is then analyzed to check the distribution of benzaldehyde, benzyl alcohol **3a** and benzoic acid **4a** by GC. The results obtained are shown in **Table 1**.

Table 1. Catalytic activity of various acid catalysts



Entry	Catalyst	Conv. 1a (%)[a]	Sel. 2a (%)[a]
1	-	-	-
2	H_2SO_4	54	11
3	CH_3SO_4	47	14
4	CF_3SO_4	50	30
5	Amberlyst IRA400	1	84
6	Nafion NR50	6	78
7	Aquivion PW66S	6	91
8	Aquivion D66-20BS	6	90
9	Silica	-	-
10	Mesoporous silica[b]	-	-
11	$-(C_6H_4)-SO_3H@SiO_2$	3	92
12	$-(CH_2)_3-SO_3H@SiO_2$	6	94
13	$-(CF_2)_3-SO_3H@SiO_2$	13	97
14	Aquivion@AM-SiO_2	38	76
15	Aquivion@MS-SiO_2[c]	46	98
16	Aquivion@NP-SiO_2	21	95

Reaction conditions: toluene (10 mmol), 30% aqueous H_2O_2 (1 ml, 10 mmol), acid catalyst (1 mol% for homogeneous acids, 100 mg for solid ones), under N_2 at 110 °C; [a] by GC; [b] prepared previously according to literature, (ref. 43); [c] obtained through impregnation of the polymer dispersion on previously-made mesoporous silica.

By carrying out this process, the oxidation of toluene to benzaldehyde took place with modest conversion and poor selectivity using homogeneous sulphonic acid (entries 2-4 in Table 1). Trying various sulphonic acid resins (entries 5-8) the reaction is slow but selectivity proved satisfactory. We then switched to sulphonic acids supported on silica (entries 11-13), which were previously prepared in laboratory [45]. Materials presenting phenylsulphonic or propylsulphonic pendants did not show an increased catalytic activity (3% and 6%, entries 11-12). A fluorinated organic tether proved more effective instead (13%, entry 13). Furthermore, **2a** formed almost exclusively in this case, selectivity being 97%. This results suggested that the perfluorinated chain could have a positive role on reactivity and we thus prepared new materials to test this hypothesis.

The combination of a perfluorinated Aquivion sulphonic acid with silica proved decisive.

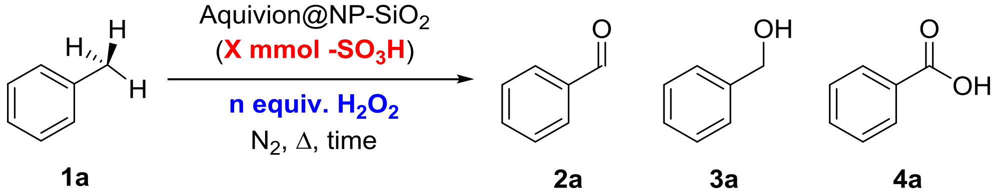
We adapted different literature procedures on Sol-Gel preparation of amorphous or mesoporous silica frameworks thanks to an ammonium template [43], adding a water-based polymer dispersion to the gelating mixture.

The resulting hybrid material gave an encouraging results (38%, 46% and 21%, entries 13-15). No reaction took place without either the oxidant or the catalyst or in presence of only silica.

After these interesting preliminary results, we decided to optimize parameters such as reaction temperature, quantity of catalyst and reagent molar ratio, choosing Aquivion@ NP-SiO_2 as model catalyst.

Several results obtained are shown in **Table 2**.

Table 2. Catalytic activity of Aquivion@NP-SiO_2 under different conditions



Entry	Conv. 1a (%)[a]	Sel. 2a (%)[a]
1[b]	3	91
2[c]	36	58
3[d]	47	99
4[d][e]	12	81
5[d][f]	66	97

Reaction conditions: toluene (10 mmol), 30% aqueous H_2O_2 (1 ml, 10 mmol), 100 mg of catalyst, under N_2 at 110 °C for 24 hours; [a] by GC; [b] at 90 °C; [c] at 130 °C; [d] with 5 mmol of H2O2; [e] with 50 mg of catalyst (0.013 mmol –SO_3H); [f] with 200 mg of catalyst (0.053 mmol -SO_3H).

The yield decreased to 3% (entry 1) by lowering the reaction temperature to 90 °C. On the contrary, raising it to 130 °C provided a dramatic drop in selectivity (down to 58%, entry 2). Gratifyingly, reduction of the amount of oxidant to 5 mmol increased the yield of **2a** to 47% (entry 3). A lower amount of catalyst had a negative effect (10%, entry 4). The best result was obtained using 200 mg of catalyst (64%, entry 5), which nonetheless correspond approximately to 1 mol% of sulphonic groups as determined by titration.

Selectivity towards **2a** remained almost complete in this case (97%), **3a** and **4a** forming in traces only (around 1% each).

Selectivity falls down by replacing H_2O_2 with organic peroxide as *tert*-butyl hydroperoxide or di-*tert*-butyl peroxide, benzoic acid becoming the main product.

In the same optimized reaction conditions, the material denominated Aquivion@MS-SiO_2 showed a bit higher results: 80% of **1a** conversion and 99% of **2a** selectivity.

By monitoring the course of the reaction over time with both catalyst (**Figure 1**), we noticed that during the first two hours the reaction is slow. This is consistent with a heterogeneous catalyzed reaction.

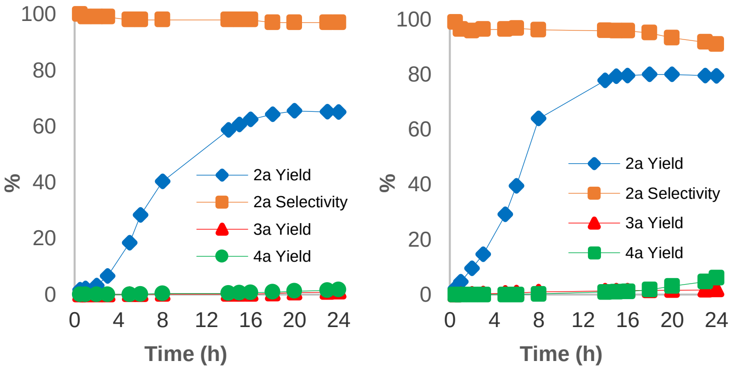


Figure 1. Yield and selectivity in function of the reaction time: on the left with Aquivion@NP-SiO_2, on the right with Aquivion@MS-SiO_2

In both cases, the conversion raised then almost linearly up to about 18 hours before reaching a plateau when the concentration of the oxidant faded. Throughout the experiment with Aquivion@NP-SiO_2, the selectivity towards **2a** remained always steady (>96%). In this case traces of both **3a** and **4a** appeared from the beginning and did not increased further. Instead, with Aquivion@MS-SiO_2, the selectivity to **2a** starts to fall slowly but steadily after 14 hours of reaction, while, as a result, increases the yield to **3a** and **4a**.
This observations suggest that the second catalyst goes probably towards a deactivation and that the formation of these side-products is due to mechanisms different than that leading to **2a**.

Stability and reusability of the catalysts were assessed recovering the solids acids by filtration on Büchner funnel at the end of the reaction, washing with 10 ml of ethyl acetate, drying and repeating the oxidation test in the same conditions (**Figure 2-3**).

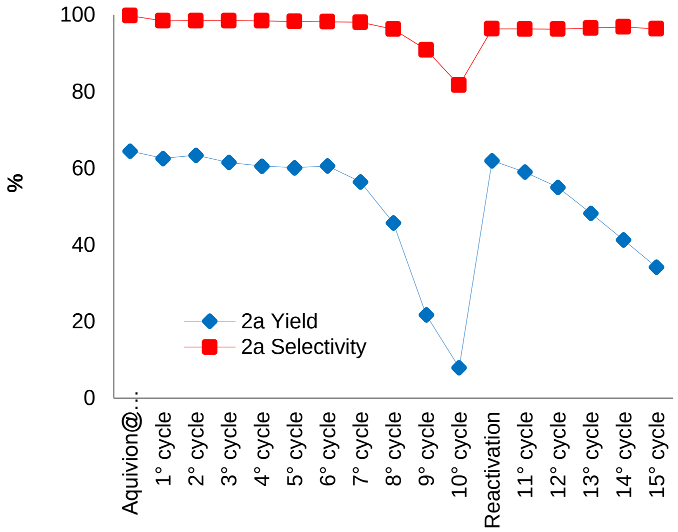


Figure 2. Aquivion@NP-SiO_2 reuse

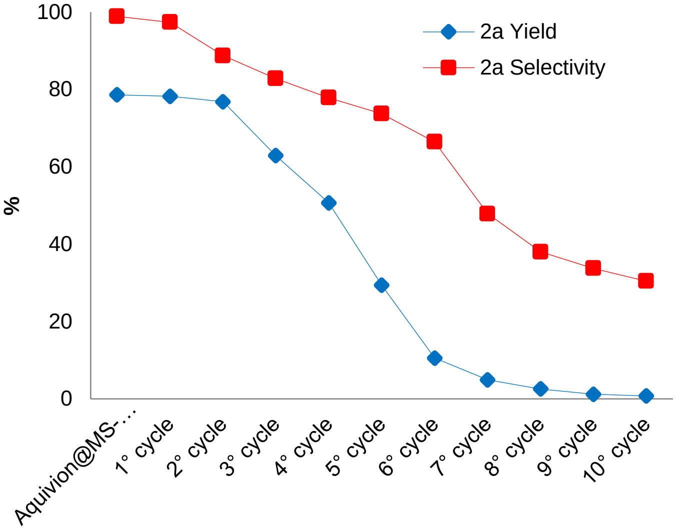


Figure 3. Aquivion@MS-SiO_2 reuse

The Aquivion@NP-SiO_2 exhibited a constant activity until the 7th run (61% yield) before reaching out to progressive inactivation (56, 46 and 22% respectively, cycle 8-10 in **Figure 2**). In all cases, selectivity remained excellent (>96%).

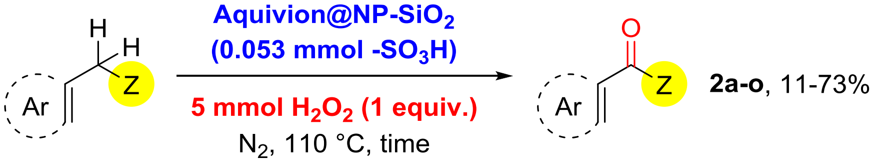
On the other hand, Aquivion@MS-SiO_2, showed a lower reusability and yet after 2nd cycle, there was a drop in yield, and between 2nd and 6th cycles decreases considerably. From the 7th cycle, the catalyst appears to be virtually inactive (**Figure 3**). This trend is probably due to the different structures of the two materials: Aquivion@MS-SiO_2 has a mesoporous structure that is more brittle than the nanoparticle of the Aquivion@NP-SiO_2, in batch conditions.

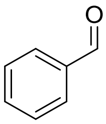
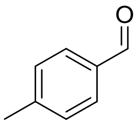
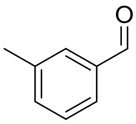
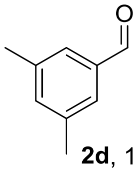
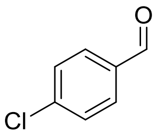
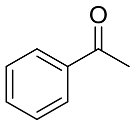
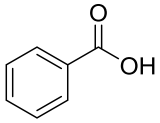
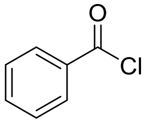
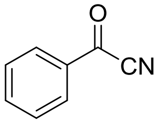
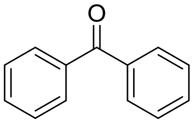
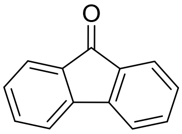
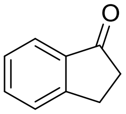
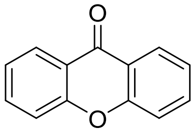
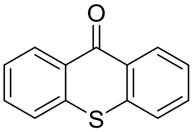
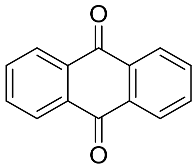
The recovered Aquivion@NP-SiO2 material seemed still macroscopically identical, but titration showed that the used material presented a tiny residual amount of Brönsted acid sites. We thus treated the inactivated material with an excess of 1M H_2SO_4 solution in ethanol. This restored its original acidity (0.267 mmol H^+/g) and delivered **2a** in 62% yield repeating our model reaction (cycle 11th).

This results further suggest that sulphonic groups of the heterogeneous material do not leach, that are the active sites of the catalyst and that the structure of the material also plays a role in catalytic activity e robustness. Although the reactivated catalyst showed a more rapid deactivation than the fresh one (cycle 12th-15th), displayed chemical stability indicates that present material can easily trigger the selective oxidation of hydrocarbons for at least 10^3 turnovers, outmatching most of their metal-based peers [39-43].

The scope and general applicability of this specific oxidation process with respect to various aromatic compounds with benzylic C-H methylenes were then investigated (**Table 3**).

Table 3. Reaction scope



 **2a**, 63% **(99%)**	 **2b**, 58% **(97%)**	 **2c**, 55% **(99%)**	 **2d**, 13% **(88%)**	 **2e**, 5% **(100%)**
 **2f**, 11% **(100%)**	 **4a**, 41% **(67%)**	 **2h**, 22% **(89%)**	 **2i**, 48% **(92%)**	 **2j**, 40% **(95%)**
 **2k**, 43% **(75%)**	 **2l**, 67% **(89%)**	 **2m**, 70% **(98%)**	 **2n**, 73% **(73%)**	 **2o**, 70% **(97%)**

Reaction scope, conditions as Table 2, entry 6; isolated yields and selectivity in to the brackets.

Toluene could be replaced by xylenes, which were selectively mono-oxidized to the corresponding product **2b-c** (**Table 3**) in good yields (58-55%). Mesitylene **1d** was the least reactive of the series, probably for its steric hindrance, and gave selective monofunctionalization (**2d**, 13% yield).

Halogenated toluenes, such as **1e**, afforded products in low yields (**2e**, 5%). Ethylbenzene gave exclusively acetophenone (**2f**), albeit in 11% yield. In all cases, selectivity remained almost complete (>95%). The reaction of benzyl alcohol provided benzoic acid (**4a**, 41%) as main product (**Figure 4**). We detected **2a** only in low yield (around 10%), and probably it is not an intermediate in this reaction.

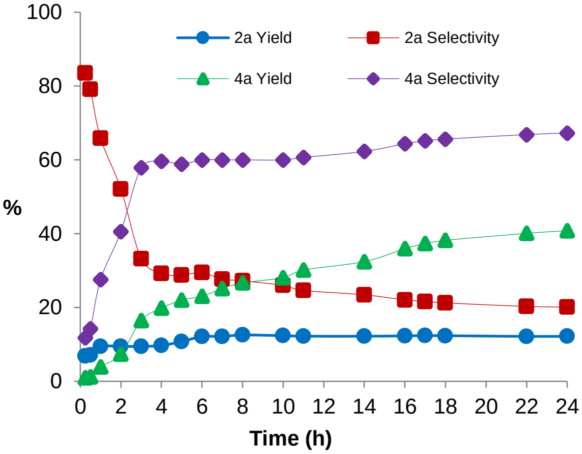


Figure 4. Reaction of **1g** versus time

This suggest that present formal 4-electrons oxidation of benzylic methylenes to carbonyls does not preceded through two separate sequential reactions.

To confirm this hypothesis we tested other substituted benzylic methylenes. Almost beyond our expectations, benzyl chloride gave indeed benzoyl chloride (**2h**, 22%). The nitrile group is similarly tolerated, as witnessed by retrieving 48% of **2i**. Most surprisingly, selectivity remained excellent in both cases (89% and 92% respectively). Other carbo-substituted benzylic derivatives followed suite, delivering the corresponding ketones with interesting yields (**2j-l**, 40-67%). Polyheterocycles could be similarly accessed (**2m-n**, 70%). Taken together (**2h-2n**), these results suggest that benzyl radicals can be initially formed [46].

During the reaction, we did not detect any intermediate of toluene oxidation so we performed further experiments to get insights on the reaction mechanism (**Figure 5**).

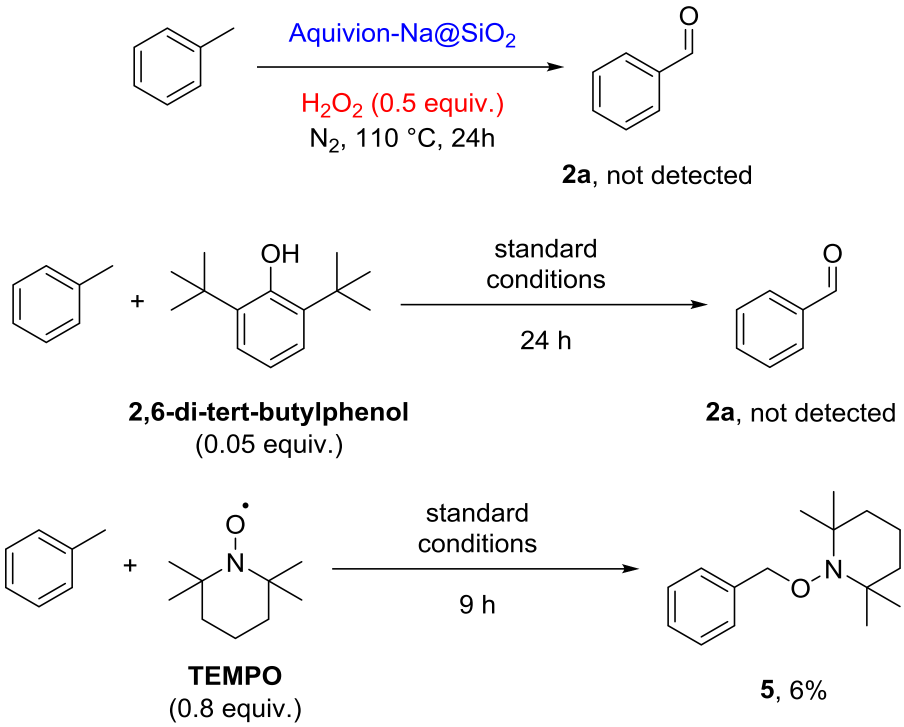


Figure 5. Mechanism probes

We exclude any significant leaching from the solid catalyst by trying the Sheldon test and not observing any further conversion of the filtrate [47].

To verify that the polyfluorinated structure of the catalyst was not degraded during the reaction, the organic and the aqueous phase were analyzed for find any fluoride in solution. In organic phase did not detect the presence of organic fluoride, while the one found in the aqueous phase (2 mmol/ l) was of little importance. Most likely due to very fine traces of heterogeneous catalyst particles dispersed in the water solution.

We carried out ICP-analysis on a freshly prepared material to quantify transition-metal traces commonly able to catalyze redox processes (**Table 4**).

Table 4. ICP analyses on metal contaminants (ppm)

Metal	Aquivion@ NP-SiO_2	Recycled Aquivion@ NP-SiO_2	Aquivion-Na^+ @NP-SiO_2
Cd	<2.5	<10	<1
Co	<2.5	<10	<1
Cr	<2.5	<10	7
Cu	8	37	6
Fe	19	22	16
Mn	<2.5	<10	<1
Mo	<2.5	<10	<1
Ni	<2.5	<10	9
Pb	<2.5	12	5
V	<2.5	<10	<1
Zn	34	66	8

For all quoted metals, the obtained results showed values lower than 10 ppm, except for iron and zinc (19 ppm and 34 ppm). Analysis on the barely inactive material upon nine recycles showed slightly higher values for all of them. This is likely due to concentration of reagent contaminants. To exclude the involvement of these metal traces in catalysis, we treated therefore our fresh material with an excess of aqueous NaOH solution. The resulting solid did not exhibit any protic acid sites and ICP-analysis showed metal contents close to previous ones. However, the treated material was completely inactive (**Figure 5**, top). This shows that toluene oxidation to **2a** is triggered by sulphonic acid groups. Toluene conversion is inhibited in presence of 0.05 equiv. of 2,6-di-*tert*-butylphenol. Using 0.05 and 0.1 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), conversion of **1a** was 13% and 27% respectively. Reactivity was completely quenched with 0.5 equiv. These results strongly suggest that present oxidation proceeds through a radical mechanism.

Warming the mixture with TEMPO for 9 hours confirmed this hypothesis. We were indeed able to isolate recombination product **5** (6%, **Figure 6a-b**).

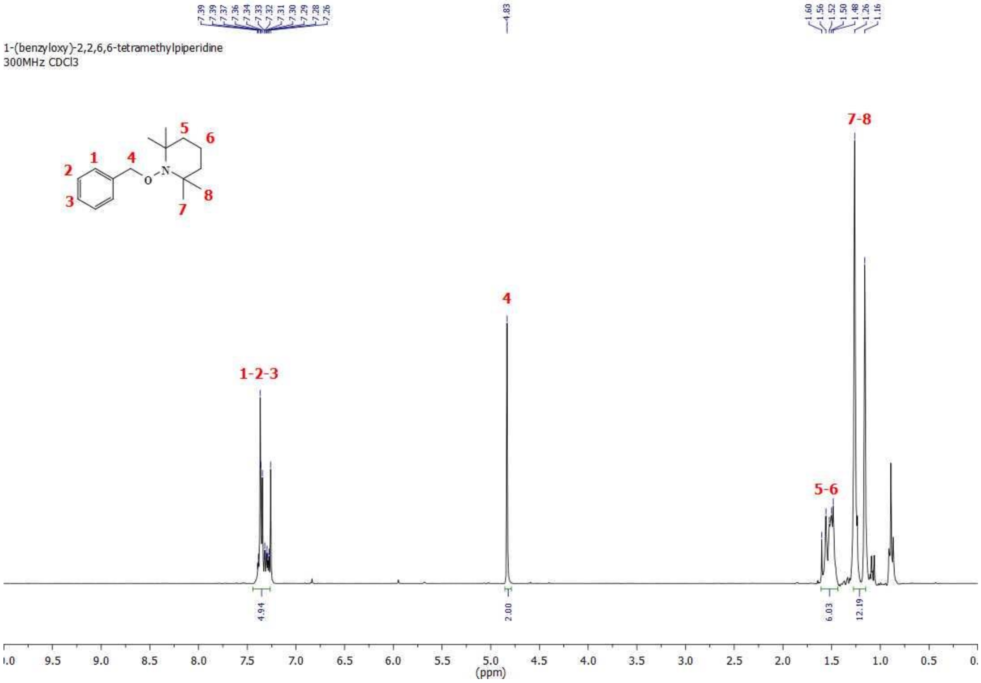


Figure 6a. ^{1}H-NMR spectra of recombination product **5**.

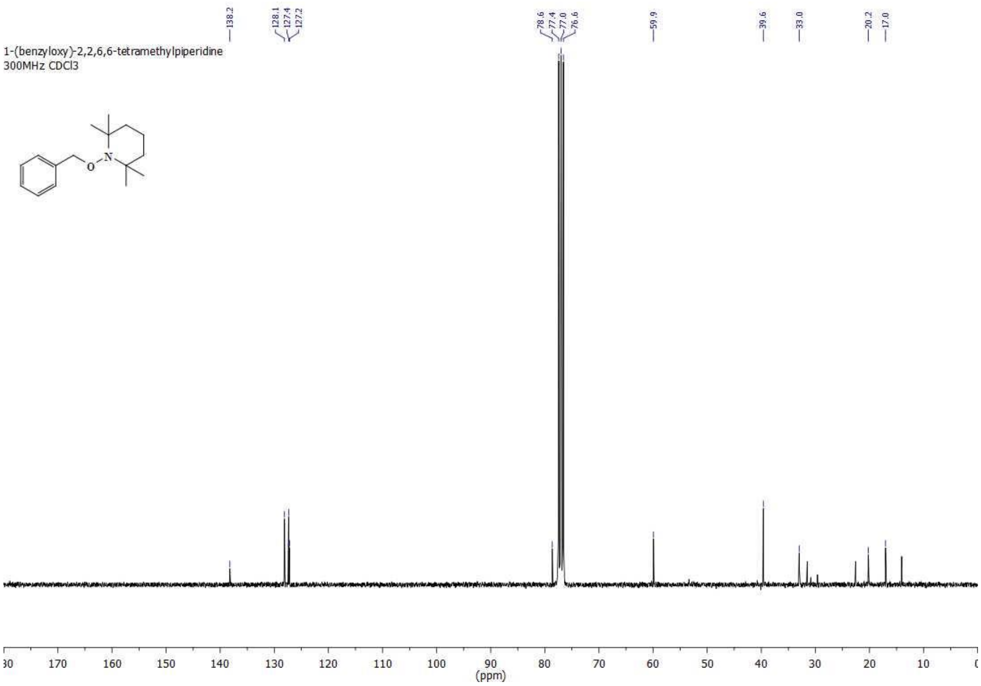


Figure 6b. ^{13}C-NMR spectra of recombination product **5**.

This confirmed that benzyl radicals are intermediates of these reactions.

On the basis of the aforementioned observations, we propose a plausible reaction mechanism in **Figure 7**.

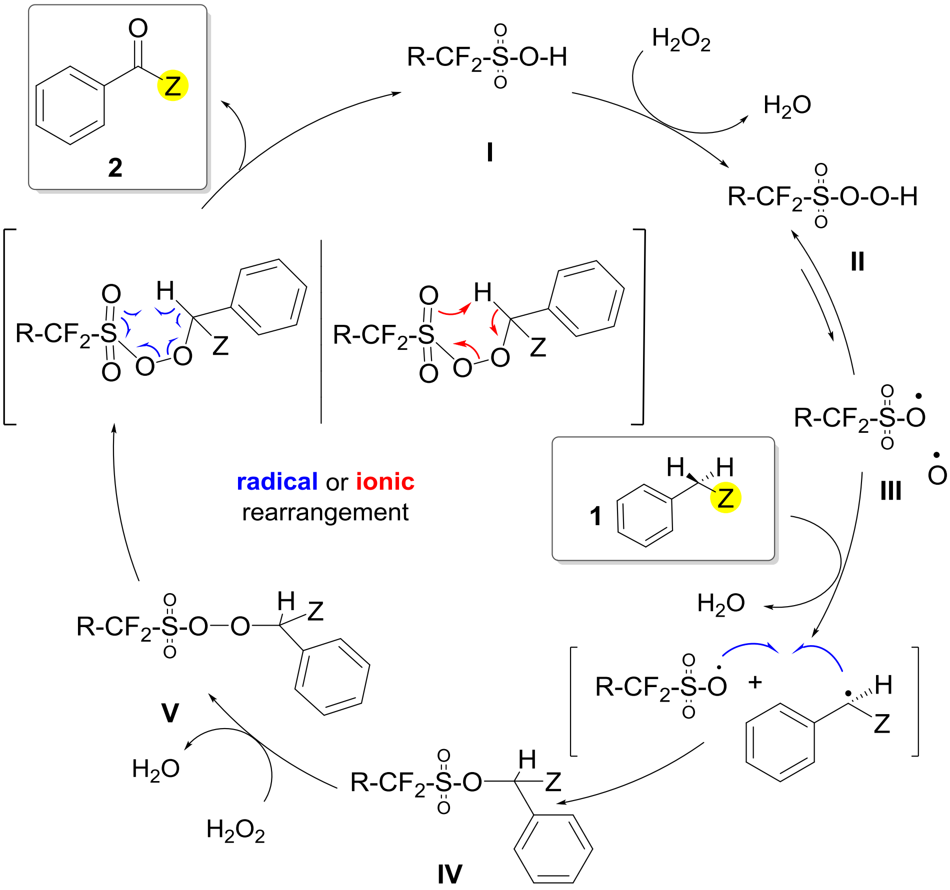


Figure 7. Possible reaction mechanism.

The sulphonic acid **I** could be oxidized to the corresponding peracid **II** by hydrogen peroxide [48]. Homolytic severance of the labile O-O bond would then yield a hydroxyl radical together with a sulphoxyl one (**III**), which is likely stabilized by its perfluorinated backbone [49]. The hydroxyl radical subtracts a hydrogen atom from **1** to yield a water molecule and a benzylic radical [50]. We expect that the latter recombines with **III** on the surface of the heterogeneous material. A second H_2O_2 molecule would then react with the resulting diamagnetic species **IV** providing **V**. The former is more electron rich than **II** thanks to its benzyl fragment. This in turn should make this peroxidation step easier, which might represent the key of the observed selectivity for this sequence. **V** eventually liberates **2** and regenerates the acid site **I**, either through a radical or an ionic rearrangement.

3.3 Conclusion

In conclusion we have reported a metal-free catalytic method for the selective oxidation of hydrocarbons featuring benzylic methylenes to the corresponding carbonyls. Narrowly dispersed silica nanoparticles decorated with polymeric perfluorinated sulphonic acids proved robust catalyst to trigger this formal 4-electrons oxidation selectively over a broad range of substrates. This combines with the use of a sustainable oxidant and the absence of any other additives to provide an interesting alternative to the synthetic toolbox.

3.4 Experimental section

General procedure for the synthesis of **2**

Gas-chromatographic analysis were accomplished on a Agilent Technologies 7820A GC System equipped with FID detector and column Agilent Technologies 19091J 413 by 30mX0.32mm and GC-MS analysis on a gas chromatograph Agilent Technologies 6890N Network GC System equipped with a detector quadrupole Agilent Technologies 5973 Network Mass Selective Detector and column Fused Silica Capillary Column by 30mX0.25mm.

200 mg of Aquivion@NP-SiO_2 were added to a sealed tube. The vessel underwent at least three vacuum/Ar cycles. The substrate (10 mmol) and 30% aqueous hydrogen peroxide (5 mmol) were sequentially added *via* syringes. The suspension was put under stirring and warmed at 110 °C for 18 hours. Upon cooling to room temperature, the catalyst was filtered and

the remaining biphasic layer transferred to a funnel. The organic layer was collected and analyzed with by GC and NMR. Technically pure products (>90% pure) can be obtained by concentration of the organic phase, essentially by evaporation under reduced pressure of unreacted starting material (which can be in principle thus recycled). Spectroscopically pure products were obtained by flash chromatography on silica gel. They were subsequently analyzed with GC-MS, ^{1}H-NMR and ^{13}C-NMR.

Characterization of products

(2a)
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.89-7.79 (m, 2H), 7.65-7.57 (m, 1H), 7.50 (t, *J* = 7.4 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 192.2, 136.3, 134.3, 129.6, 128.9

(2b)
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 191.9, 145.5, 134.1, 129.7, 129.6, 21.8

(2c)
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.69-7.58 (m, 2H), 7.44-7.36 (m, 2H), 2.40 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 192.5, 138.8, 136.5, 135.2, 129.9, 128.8, 127.1, 21.1

(2d)
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.49 (s, 2H), 7.27 (s, 1H), 2.40 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 192.8, 138.7, 136.6, 136.2, 127.5, 21.0

(2e)
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.85-7.79 (m, 2H), 7.54-7.46 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 190.8, 140.9, 134.7, 130.9, 129.4

(2f)
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.99-7.88 (m, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 2.58 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 198, 137, 133, 128.4, 128.2, 26.5

(4a)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.18-8.08 (m, 2H), 7.68-7.59 (m, 1H), 7.48 (dd, *J* = 4.7, 10.5 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.5, 133.8, 130.2, 129.4, 128.5

(2h)

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16-8.05 (m, 2H), 7.74-7.62 (m, 1H), 7.50 (dd, J = 4.9, 10.7 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.2, 135.2, 133.1, 131.3, 128.9

(2i)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.82-7.73 (m, 1H), 7.60 (dd, *J* = 4.8, 10.7 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.8, 136.8, 133.2, 130.4, 129.5, 112.6

(2j)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 3.3, 5.2 Hz, 4H), 7.65-7.53 (m, 2H), 7.47 (dd, *J* = 4.5, 10.2 Hz, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 196.6, 137.5, 132.3, 129.9, 128.2

(2k)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.46-7.34 (m, 4H), 7.22 (ddd, *J* = 2.5, 6.1, 7.4 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 193.7, 144.3, 134.5, 134.1, 128.9, 124.1, 120.2

(2l)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.63-7.51 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.41-7.29 (m, 1H), 3.19-3.06 (m, 2H), 2.75-2.59 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 207, 155.1, 137, 134.5, 127.2, 126.6, 123.6, 36.1, 25.7

(2m)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.35 (dd, *J* = 1.4, 8.0 Hz, 2H), 7.75-7.65 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 177.1, 156.1, 134.7, 126.6, 123.8, 121.8, 117.9

(2n)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.62 (d, *J* = 8.1 Hz, 2H), 7.66-7.56 (m, 4H), 7.48 (ddd, *J* = 1.6, 6.7, 8.2 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 179.9, 137.2, 132.2, 129.8, 129.2, 126.3, 126

(2o)
^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.36-8.29 (m, 4H), 7.85-7.79 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 183.2, 134.1, 133.5, 127.2

(5)
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38-7.29 (m, 5H), 4.8 (s, 2H), 1.59-1.47 (m, 6H), 1.26 (s, 6H), 1.16 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 138.2, 128.1, 127.4, 127.2, 78.6, 59.9, 39.6, 33, 20.2, 17.0

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4 Oxidative dimerization of anilines with sulphonic acids catalysts

4.1 Introduction

Aromatic azo-compounds are ubiquitous motifs very important in many areas of science. Azo compounds display crucial properties for important applications and are widely used in the chemical industry as dyes and pigments [1], food additives, indicators [2], radical reaction initiators [3] and therapeutic agents [4]. In addition, azo compounds have shown promise in electronics [5] and drug delivery [6]. Moreover, azobenzenes recently have been targeted for potential applications in areas of nonlinear optics, optical storage media, chemosensors, liquid crystals [7], photochemical molecular switches [8], molecular shuttles [9], nanotubes [10] and in the manufacture of protective eye glasses and filters [11]. The light driven reversible isomerization of azobenzenes between *cis* and *trans* forms makes them excellent candidates to modulate the relative movement of different moieties. For instance, the motion of one molecule containing an azobenzenes group is able to control the movement of a complementary substrate non-covalently bound to the azobenzenes fragment [12].

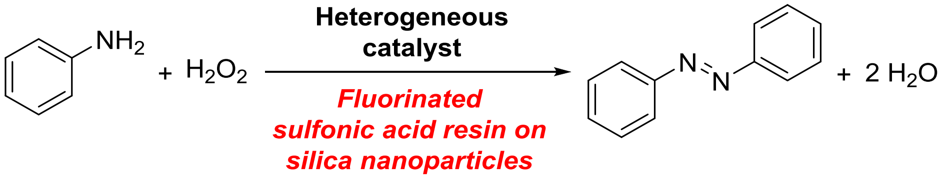
Conventional methods for the formation of aromatic azo-compounds involve the use of stoichiometric amounts of nitrite salts ($NaNO_2$) or toxic oxidants and proceed via diazonium o nitrosobenzene intermediates [13]. Other two historical synthetic routes to prepare azo compounds are the Mills reaction [14, 15, 16, 17, 18], namely the reaction between aromatic nitroso derivatives and anilines, and the Wallach reaction [19-21], that is the transformation of azoxybenzenes into 4-hydrozy substituted azoderivatives in acid media.

Catalytic pathways can make these conventional processes facile and more selective. However, the existing systems have several drawbacks, such as lower yields, undesirable overoxidation products, limited functional group compatibility, the presence of additives, the use of harsh reaction conditions and poor reusability of the catalyst.

In the following years, many important attempts were made to synthesis azo-derivatives in good yields, for example, by the use of a CuBr/pyridine/O_2 reaction system [22], a photocatalytic pathway in the presence of Au/ZrO2 [23] and Pt or Pd nanowires in the presence of KOH [24]. However, the use of precious metals, high pressure and base additives make these processes industrially and environmentally unfriendly. Therefore, the development of cost-effective, efficient, heterogeneous catalysts for the synthesis of aromatic azo-compounds under mild reaction conditions is highly desirable.

The development of organic frameworks able to mimic the versatility and robustness of transition metal catalysts has been witnessed by a series of milestones in recent years [25]. The involvement of acids as catalysts to trigger redox processes are scarce in organic synthesis [26].

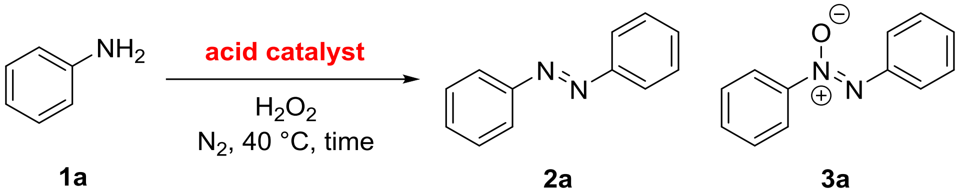
We report herein that our catalytic system based on supported perfluorinated sulphonic acid Aquivion can catalyze the oxidative dimerization of anilines using hydrogen peroxide as clean oxidant. The reactivity can be exploited for the synthesis of *trans*-azobenzenes, showing large functional groups tolerance. Also in this case, Aquivion@NP-SiO_2 has been shown very efficient and robust catalyst, representing therefore a valuable tool complementary to existing metal-based methods.



4.2 Results and discussion

In an initial experiment, we observed formation of traces of *trans*-diphenyldiazene (**2a**, 15%) upon treatment of aniline (**1a**, 1 mmol) with 1 equiv. of hydrogen peroxide in the presence of 1 mol% of trifluoromethansulphonic acid at 60 °C for 24 hours. Under these conditions, conversion of **1a** did not reach completion (90%) and azoxy product **3a** was the main product of the reaction (77%). Reasoning on the synthetic interest towards products **2**, we varied some reaction parameters to achieve a selective reaction. We immediately noticed that the presence of oxygen favors the formation of **3a** and we thus performed the reactions under N_2 for optimization. Upon preliminary screening, we observed that the reaction can easily be performed on 10 mmol scale by gently warming freshly degassed solutions of **1a** and H_2O_2 at 40 °C in a Schlenk-type flask in the presence of the desired sulphonic acid catalyst. The effect of the catalyst on the formation of **2a** is presented in **Table 1**.

Table 1. Catalytic activity of various acid catalysts



Entry	Catalyst	Conv. 1a (%)[a]	Sel. 2a (%)[a]
1	-	10	24
2	H_2SO_4	91	12
3	CH_3SO_3H	88	7
4	CF_3SO_3H	90	30
5	$-(CH_2)_3-SO_3H@SiO_2$	85	7
6	$-(C_6H_4)-SO_3H@SiO_2$	66	18
7	$-(CF_2)_3-SO_3H@SiO_2$	78	47
8	Nafion NR50	89	38
9	Aquivion PW66-S	93	42
10	Aquivion@Al_2O_3	97	15
11	Aquivion@NP-SiO_2	98	73

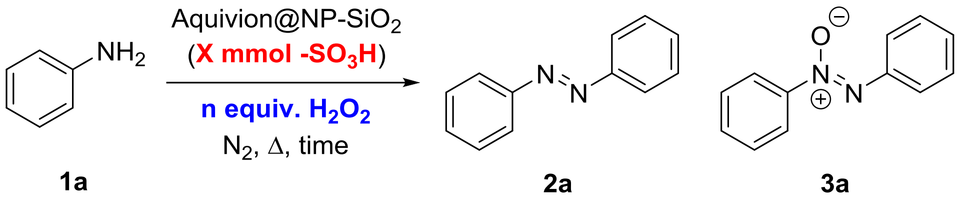
Reaction conditions: aniline (10 mmol), 30% aqueous H_2O_2 (1 ml, 10 mmol), acid catalyst (1 mol% for homogeneous acids, 250 mg for solid ones), under N_2 at 40 °C; [a] by GC.

Aniline oxidation occurs smoothly with simple homogeneous acids (entries 2-4). Sulphuric acid leads however to extensive decomposition (entry 2). Methanelsulphonic and triflic acid ensured high conversion of **1a**, although **3a** was the main product in these cases (74 and 66% respectively). We then reasoned to smooth the reactivity of the acid catalyst by testing heterogeneous sulphonic acid derivatives. Solid acid presenting either propylsulphonic or phenylsulphonic groups did not increase the selectivity towards **2a** (7 and 18%, entries 5-6). On the contrary, a fluorinated organic tether proved beneficial (entry 7, 47% of **2a**). Perfluorinated polymeric resins Nafion and Aquivion allowed to retrieve **2a** with higher selectivity compared with their homogeneous peers (38 and 42%, entries 8-9). This trend could confirm a positive effect exerted by a fluorinated organic backbone on the reaction. Also in this case, the combination of fluorinated commercial resins with a suitable inorganic support proved decisive. While the use of alumina did not steer the outcome (15%, entry 10), product **2a** become the mayor species using silica as inorganic support (73%, entry 11). Conversion of **1a** remained below 10%, delivering exclusively **3a**, without any catalyst (entry 1). Product **2a** was not detected in the presence of bare silica. Similarly, **2**a did not form replacing H_2O_2 with stronger organic peroxides as *tert*-butyl-hydroperoxide and di-*tert*-butylperoxide.

After these interesting preliminary results, we decided to optimize parameters such as reaction temperature, quantity of catalyst and reagent molar ratio, choosing Aquivion@ NP-SiO_2 as model catalyst.

Several results obtained are shown in **Table 2**.

Table 2. Catalytic activity of Aquivion@NP-SiO2 under different conditions



Entry	Conv. 1a (%)[a]	Sel. 2a (%)[a]
1[b]	24	92
2[c]	99	52
3[d]	100	23
4[e]	98	46
5[f]	98	83
6[g]	96	93

Reaction conditions: aniline (10 mmol), 30% aqueous H_2O_2 (1 ml, 10 mmol), 250 mg of catalyst, under N_2 at 40 °C for 24 hours; [a] by GC; [b] at room temperature; [c] at 60 °C; [d] at 80 °C; [e] with 2 equiv. H_2O_2; [f] with 100 mg of catalyst (0.027 mmol $-SO_3H$); [g] with 50 mg of catalyst (0.013 mmol $-SO_3H$).

Carrying out the reaction at room temperature the **1a** conversion was low, but the selectivity to **2a** was very good (entry 1).

By increasing the temperature (to 60 and 80 °C, entry 2-3), a decisive rise of **1a** conversion was observed but also a drastic drop of selectivity to **2a** in favor of the by-product **3a**.

The selectivity also sunk to 46% performing the reaction with 2 equiv. of oxidant (entry 4). Further increase of the selectivity with almost quantitative conversion was achieved reducing the amount of catalyst (entries 5-6, 83 and 93% respectively). We have also conducted several tests in presence of different polar solvents (DMF, MeCN, EtOAC, MeOH), but the main product was always **3a.**

Remarkably, considering that a supported organic catalyst was employed, the best result was obtained with as low as 0.26 mol% of sulphonic acids groups.

Under the best reaction conditions identified in the previous steps, we analyzed the progress of reaction over time (**Figure 1**).

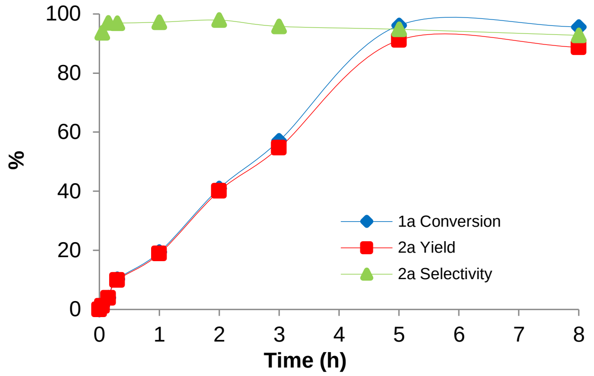


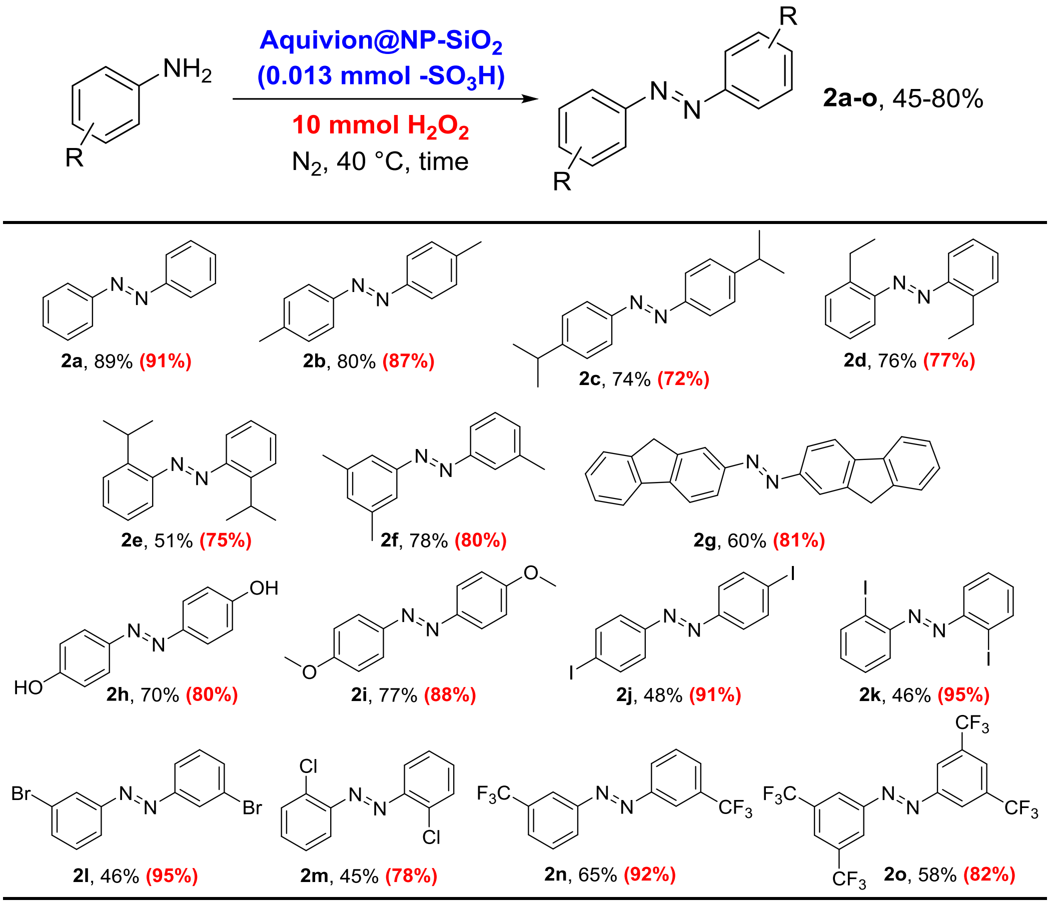
Figure 1. Conversion, yield and selectivity in function of the reaction time

The reaction exhibited a very high selectivity starting from the first minutes, while the best results in terms of **1a** conversion and **2a** yield and selectivity were obtained after 6 hours.

After six hours the reaction reaches a plateau and the values remained almost unaltered.

So, with best conditions in our hands (**Table 2**, entry 6), we then studied the scope of this reaction (**Table 3**).

Table 3. Reaction scope



Reaction scope, conditions as Table 2, entry 6; isolated yields and selectivity into the brackets.

The phenyl ring of aniline can be decorated with various alkyl substituents in the *ortho*-, *meta*- and *para*- positions delivering the corresponding products **2b-e** in good yields (74-80%). Aniline **1e** is the least reactive of the series, likely owing to the presence of a bulky isopropyl group *ortho* to nitrogen, but yield nonetheless **2e** in 51%. The methylene group of fluorenes remains untouched, as witnessed by the isolation of **2g** in 60% yield. Unhindered hydroxyl and methoxy groups are similarly tolerated, delivering the corresponding products **2h-i** in 70 and 77% yield respectively. Switching to electron withdrawing groups, halogenated anilines could be coupled through this method, affording products in moderate yields (**2j-m**, 45-48%).

Products **2h-m** offer convenient handles for further functionalization and desymmetrization. Trifluoromethylated anilines deliver the corresponding azobenzenes **2n** and **2o** in 65% and 58% respectively.

The solid acid was recovered by filtration at the end of the reaction and the biphasic mixture was then separated in a funnel. The organic phase was washed with a 1M HCl solution (3X10 ml). This enables to recover technically pure products **2** (>90% by NMR, **Figure 2**) and the salt of the unreacted aniline from aqueous phases, which do not contain any more peroxides, likely owing the decomposition of unreacted H_2O_2.

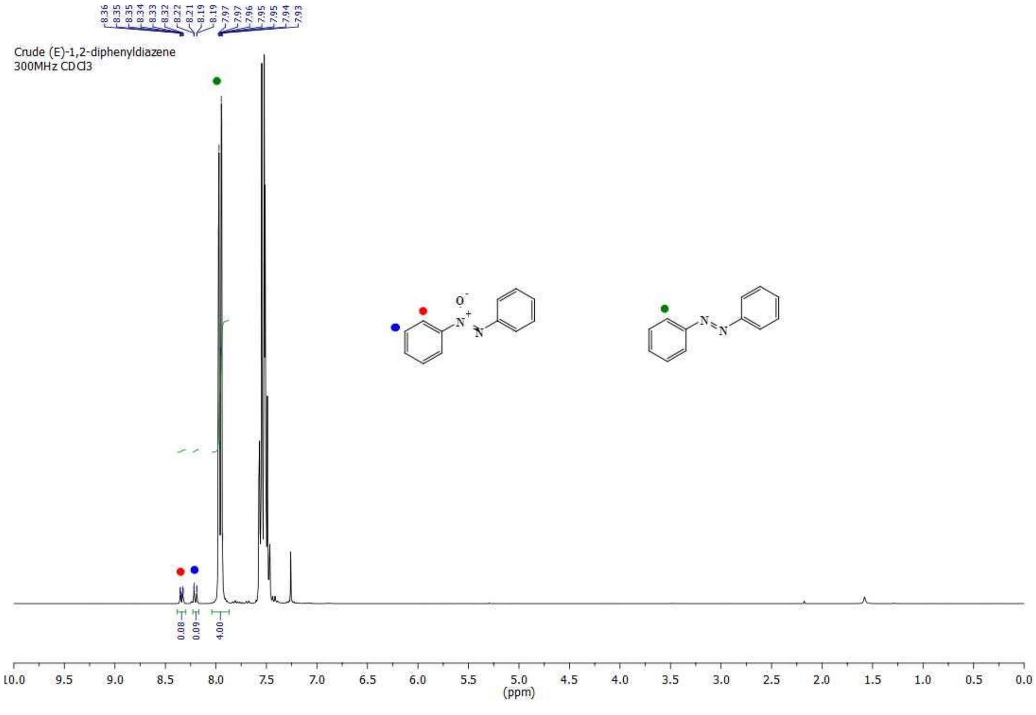


Figure 2. ^{1}H-NMR spectrum of the crude washed with a 1M HCl solution. The final result shows **2a** with a technical degree of purity (96%).

Taken together, these results show the practical and environmental viability of present method, which is inherently safe and minimizes the use of chemicals to recover products. Chromatography on silica gel affords spectroscopically pure **2** and **3** (<5% each), which could in principle led to **2** as well.

The recovered solid acid has become brown at the end of the reaction and, disappointingly, it is no longer active. Washings with solvents of different polarity had no effect. Titration showed however that the used material did not present any acid site. We reasoned that this could be due to chemisorption of byproducts with basic nitrogen atoms. We thus treated the used material with an excess of aqueous acid solution. This replenished its original acidity (0.267 mmol H^+/g), removed traces of adsorbed colored organics and, to our delight, delivered again **2a** in 88% yield repeating our model reaction.

We rule out any significant leaching from the solid catalyst by performing the Sheldon test: any further conversion of the filtrate was observed.

To ascertain that sulphonic acid groups act as catalyst at the molecular level in analogy with the former oxidation reaction (**Chapter 3**) and to their homogeneous peers (**Table 1**), we treat our material with an excess of aqueous NaOH. The resulting solid did not exhibit anymore protic acid sites, as determined by titration. It proved unable to induce formation of **2a** too (**Figure 3**). Conversion of **1a** was 35% after 24 hours at 40 °C and **3a** became the mayor product (31%). Taken together, these results strongly suggest that the oxidative dimerization of anilines to **2** is triggered by sulphonic acid groups.

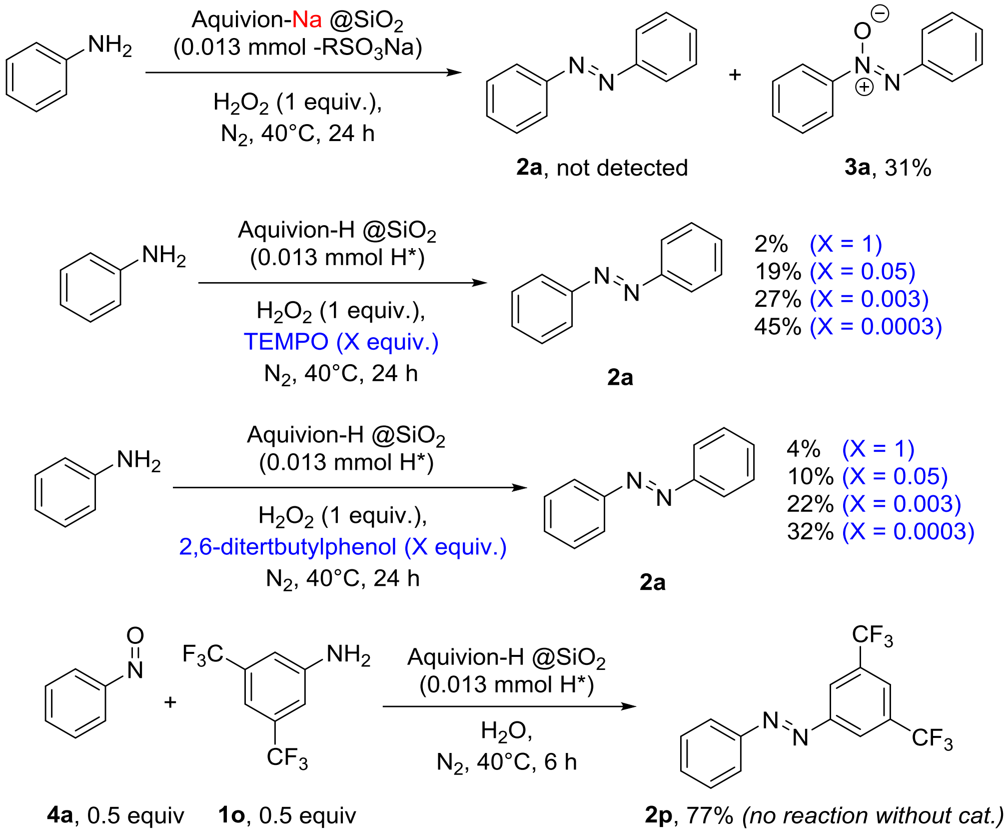


Figure 3. Mechanism probes

Conversion of **1a** remained below 5% in the presence of either 1 or 0.5 equiv. of TEMPO. The use of 0.05 equiv. enabled the formation of **2a** in 19% yield. Further reduction to 0.003 equiv. allowed to retrieve 27% of **2a**. The use of 0.0003 equiv. still had a negative effect on conversion and yield (49% and 45% respectively).

A comparable trend was observed replacing TEMPO with 2,6-di-*tert*-butylphenol.

This is in striking contrast with the smooth coupling occurred using unhindered (amino)phenols as substrates (2h, 70%, **Table 3**). These results strongly suggest the involvement of paramagnetic intermediates in these reactions. However, we did not observe any products of radical recombination in all these cases. Similarly, no trapping occurred performing the reaction with 1 equiv. of benzyldenemalonitrile as radical acceptor.

Nitrosobenzene **4a** did not react with anilines upon 24 hours at 40 °C (**Figure 3**, bottom). On the contrary, even employing the weakly nucleophilic aniline **1p**, the addition of the heterogenized sulphonic acid enabled to retrieve product **2p** in 77%. Using aniline, **2a** forms in 94% yield. These results are consistent with the intermediate formation of nitrosobenzene in these sequences. The solid acid catalyzes the formation of **2p** likely *via* nucleophilic addition of **1p** on **4a** and subsequent formal dehydration [27].

Under these conditions, product **2p** did not form replacing nitrosobenzene with either nitrobenzene or hydroxylaniline. These results reduce the likeness that these species are intermediates in present catalytic dimerization of anilines to **2**. Nitrosobenzenes are often prepared *in-situ* from the corresponding hydroxilamines [28]. Present findings could represent therefore a complementary tool to access a valuable synthetic motif from simpler reagents, namely anilines. Nitrosobenzenes are labile species in oxidizing environments and over oxidation to nitrobenzenes is indeed a recurrent side-reaction that impose the use of molar excess of precursors [28]. This could correlate with the reactivity trend observed varying the nature of the sulphonic acid derivative (**Table 1**). The heterogenization and a low molar loading might be indeed the key to slowly generate nitrosobenzene preventing undesired oxidations.

We thus performed additional experiments to try to isolate nitrosobenzene as intermediate of the reaction. By exploiting the tendency of nitrosobenzenes to sublimate, a reaction with fresh distilled aniline **1n** was conducted in a high and narrow reactor by refrigerating the upper walls. After several hours of reaction it was possible to observe a yellowish solid deposit **5a** on the walls of reactor (**Figure 4**).

Figure 4. Nitrosobenzene deposits

The solid (50 mg) was recovered from the reactor sides with a spatula, washed with water, dried on filter paper and analyzed by ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR (**Figure 5a-c**).

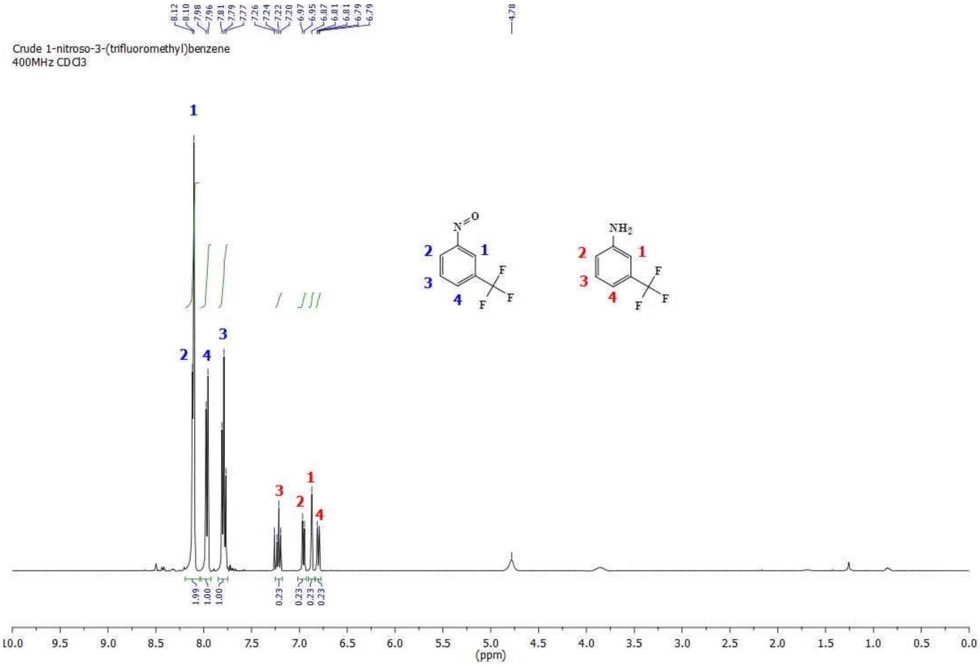


Figure 5a. NMR spectra of recovered **5a** (1-nitroso-3-(trifluoromethyl)benzene) crude

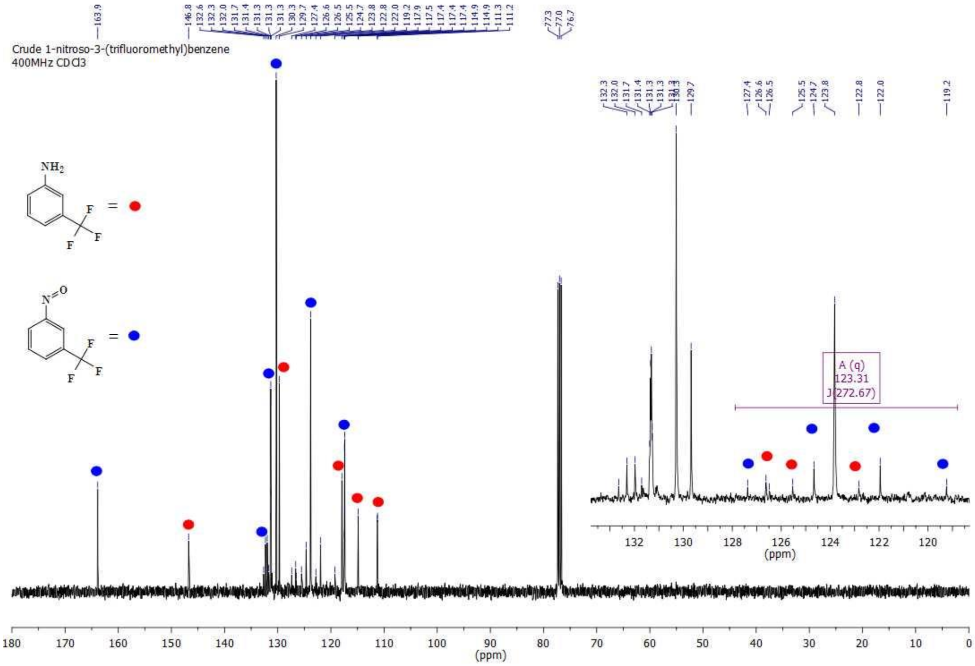


Figure 5b.

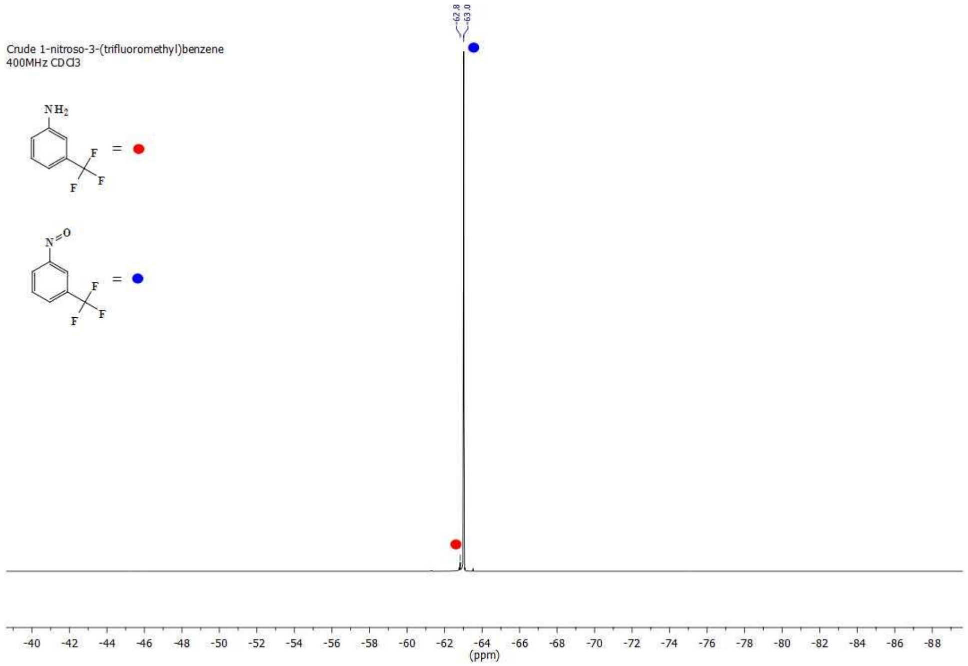


Figure 5c.

We were unable to further purify the recovered intermediate.

On the basis of these results, we propose the rationale presented in **Figure 6** as working hypothesis for the formation of *trans*-azobenzenes **2** in these sequences. The sulphonic acid **I** could be oxidized to the corresponding peracid **II** by hydrogen peroxide [29]. Homolytic cleavage of the labile O-O bond would then yield a hydroxyl radical together with a sulphoxyl one (**III**), which is likely stabilized by hyperconiugation thanks to a perfluorinated backbone [30]. The former radical abstracts a hydrogen atom from **1a** to yield a water molecule and an aminyl radical [31], which we speculate might be prone to swift recombination with **III** on the surface of the heterogeneous material. The resulting diamagnetic species **IV** would then react with a second H_2O_2 molecule, providing **V** in analogy to **II.** Its decomposition liberates nitrosobenzene **4a** and regenerates acid **I.** Nucleophilic attack of a second molecule of **1a** on **4a** and sequential dehydration by **I** eventually delivers desired product **2a** in its *trans*- form [27].

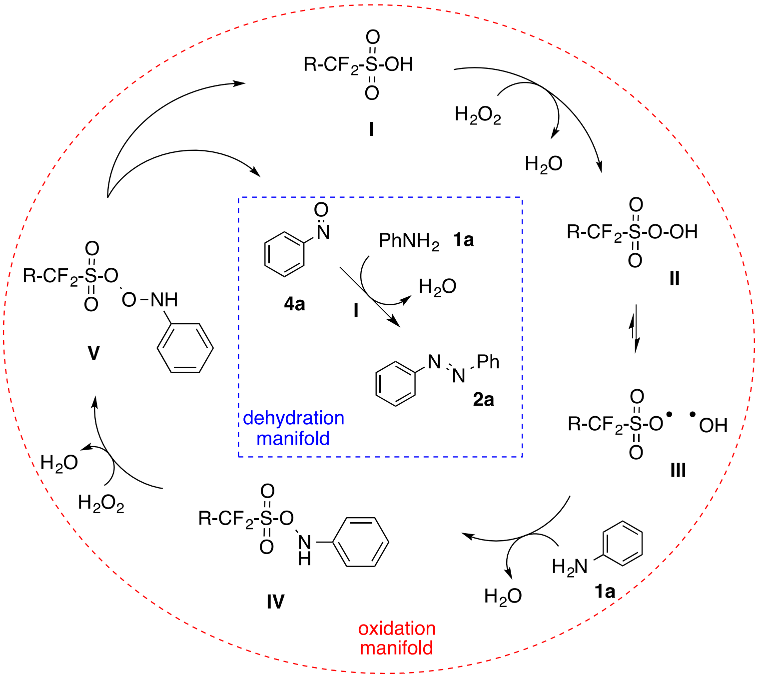


Figure 6. Possible reaction rationale

In this scenario, the sulphonic acid would play two distinct roles, triggering aniline oxidation to nitrosobenzene in the first part and then acting as dehydration catalyst in the sequential redox-neutral cycle. Present sequence would thus represent a cascade reaction [32]. To the best of our knowledge, this behavior has not been previously observed with organic acids.

We could not rule out at present stage the formation of **4a** via chain reaction. In this case, the sulphonic acid would be the initiator of the first part of the sequence. However, the significant suppression of the yield of **2a** in the presence of tiny molar amounts of radical quenchers seems at odds with a chain propagation process [33].

The low loading (0.26 mol%) and the stability of the polymeric sulphonic acid further suggest that the latter plays the role of a catalyst on the basis of present preliminary results.

4.3 Conclusion

In conclusion, we reported that sulphonic acids can catalyze the oxidation of anilines under mild conditions. Suitable solid acids steer this reactivity towards the selective formation of *trans*-diarylazenes. The method is complementary to existing strategies that requires the consumption of transition metals, organic oxidants and co-solvents. The use of stoichiometric hydrogen peroxide combined with simple work-up/purifications and broad functional group tolerance portrays the potential of these findings for future developments. Most remarkably, the polymeric acid preserved its activity for a few thousand turnovers, outmatching the robustness of most of its (metal-based) peers.

4.4 Experimental section

General procedure for the synthesis of **2**

Gas-chromatographic analysis were accomplished on a Agilent Technologies 7820A GC System equipped with FID detector and column Agilent Technologies 19091J 413 by 30mX0.32mm and GC-MS analysis on a gas chromatograph Agilent Technologies 6890N Network GC System equipped with a detector quadrupole Agilent Technologies 5973 Network Mass Selective Detector and column Fused Silica Capillary Column by 30mX0.25mm.

Fresh distilled aniline derivative (10mmol, 1 eq.) and hydrogen peroxide (10 mmol, 1 eq.) were added under argon to the catalyst (50mg) in a Schlenk-bomb type flask.

The mixture was kept under vigorous stirring at 40°C in an oil bath for at least 24 hours.

Catalyst was filtered on a thin layer of Celite using a Büchner funnel and washed with hexane or diethyl ether (3x10ml).

The resulting biphasic mixture is then separated in a funnel and the organic layer was recovered, washed with a 1M HCl solution (3x10ml) to remove the unreacted aniline, dried over Na_2SO_4 anhydrous and filtered.

The solvent was removed under vacuum and the desired product was purified by flash column chromatography on silica gel.

Characterization of products

(2a)

^{1}H-NMR: δ 8.05-8.01 (m, 4H), 7.59-7.55 (m, 6H); ^{13}C-NMR: δ 152.6, 130.9, 129.1, 122.8

(2b)

^{1}H-NMR: δ 7.83 (d, J = 8.3 Hz, 4H), 7.31 (d, J = 8.1 Hz, 4H), 2.44 (s, 6H); ^{13}C-NMR: δ 150.8, 141.2, 129.7, 122.7, 21.5

(2c)
^{1}H-NMR: δ 7.86 (d, J = 8.4 Hz, 4H), 7.37 (d, J = 8.3 Hz, 4H), 3.0 (dt, J = 6.9, 13.8 Hz, 2H), 1.31 (d, J = 6.9 Hz, 12H); ^{13}C-NMR: δ 152, 151.2, 127.1, 122.8, 34.1, 23.9

(2d)
^{1}H-NMR: δ 7.64 (d, J = 7.8 Hz, 2H), 7.41-7.37 (m, 4H), 7.32-7.27 (m, 2H), 3.21 (q, J = 7.5 Hz, 4H), 1.33 (t, J = 7.4 Hz, 6H); ^{13}C-NMR: δ 150.5, 144.3, 130.9, 129.8, 126.4, 115.6, 24.7, 16.5

(2e)
^{1}H-NMR: δ 7.72 (dd, J = 0.8, 8.1 Hz, 2H), 7.52 (m, 4H), 7.35 (ddd, J = 1.9, 6.9, 8.5 Hz, 2H), 4.28 (hept, J = 6.9 Hz, 2H), 1.46 (d, J = 7 Hz, 12H); ^{13}C-NMR: δ 150.0, 148.0, 131.0, 126.3, 126.2, 115.5, 27.7, 23.8

(2f)
^{1}H-NMR: δ 7.54 (s, 4H), 7.12 (s, 2H), 2.42 (s, 12H); ^{13}C-NMR: δ 152.9, 138.7, 132.5, 120.5, 21.2

(2g)
^{1}H-NMR: δ 8.38 (s, 2H), 8.28 (dd, J = 1.8, 8.4 Hz, 2H), 7.86 (dd, J = 4.1, 8.4 Hz, 4H), 7.63-7.60 (m, 2H), 7.44 (dd, J = 2.5, 6 Hz, 4H), 3.99 (s, 4H); ^{13}C-NMR: δ 148, 146.7, 144.8, 143.9, 139.4, 128.8, 127.4, 125.4, 123.1, 121.3, 120.4, 119.8, 36.9

(2h)
^{1}H-NMR (MeOD-d_4): δ 7.77 (d, J = 8.8 Hz, 4H), 6.92 (d, J = 8.8 Hz, 4H); ^{13}C-NMR (MeOD-d_4): δ 161.5, 147.8, 125.6, 116.9

(2i)
^{1}H-NMR: δ 7.91-7.86 (m, 4H), 7.03-6.98 (m, 4H), 3.89 (s, 6H); ^{13}C-NMR: δ 161.6, 147, 124.4, 114.4, 55.6

(2j)
^{1}H-NMR: δ 7.89-7.84 (m, 4H), 7.66-7.62 (m, 4H); ^{13}C-NMR: δ 151.7, 138.4, 124.5, 98.1

(2k)
^{1}H-NMR: δ 8.03 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.18 (t, J = 7 Hz, 2H); ^{13}C-NMR: δ 150.7, 139.9, 132.7, 129, 118.2, 103.3

(2l)

^{1}H-NMR: δ 8.06 (s, 2H), 7.90-7.87 (m, 2H), 7.62 (ddd, J = 1, 1.8, 7.9 Hz, 2H), 7.44-7.39 (m, 2H); ^{13}C-NMR: δ 153.1, 134.1, 130.5, 124.7, 124.5, 123.2

(2m)

^{1}H-NMR: δ 7.78 (dd, J = 1.8, 7.8 Hz, 2H), 7.57 (dd, J = 1.5, 7.8 Hz, 2H), 7.39 (td, J = 2.9, 6.3 Hz, 4H); ^{13}C-NMR: δ 148.7, 135.8, 132.2, 130.7, 127.4, 118.1

(2n)

^{1}H-NMR: δ 8.22 (s, 2H), 8.14 (d, J = 7.9 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.67 (7, J = 15.6, 7.8 Hz, 2H); ^{13}C-NMR: δ 152.2, 131.8 (q, J = 33.0 Hz), 129.9, 127.9 (q, J=3.7 Hz), 125.5, 123.75 (q, J = 272.5 Hz, -CF$_3$), 119.7 (q, J = 4.0 Hz); ^{19}F-NMR: δ -62.8

(2o)

^{1}H-NMR: δ 8.45 (s, 4H), 8.07 (s, 2H); ^{13}C-NMR: δ 152.1, 133,1 (q, J=34.1 Hz, -CCF$_3$), 125.3-125.0 (m), 123.6-123.2 (m), 122.9 (q, J = 272.73 Hz, -CF$_3$); ^{19}F-NMR: δ -58.2

(2p)

^{1}H-NMR: δ 8.37 (s, 2H), 8.01-7.95 (m, 3H), 7.59-7.54 (m, 3H); ^{13}C-NMR: δ 152.8, 152.0, 132.7 (q, J=33.8, -CCF$_3$), 132.5, 129.3, 123.9-123.5 (m), 123.4, 123.2-122.8 (m), 123.1 (q, J = 272.9 Hz, -CF$_3$); ^{19}F-NMR: δ -63

(3a)

^{1}H-NMR: δ 8.35-8.31 (m, 2H), 8.21-8.18 (m, 2H), 7.53 (dddd, J = 1.3, 5.4, 7.9, 9.9 Hz, 5H), 7.43-7.38 (m, 1H); ^{13}C-NMR: δ 144, 131.5, 129.6, 128.7, 128.6, 125.5, 122.3

(5)

^{1}H-NMR: δ 8.11 (d, J = 6.3 Hz, 2H), 7.97 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 8.1 Hz, 1H); ^{13}C-NMR: δ 163.9. 132.2 (q, J = 33.7 Hz, -CCF$_3$), 131.3 (dd, J = 3.4, 6.9 Hz), 130.3, 123.8, 123.3 (q, J = 272.7 Hz, -CF$_3$), 117.4 (q, J = 3.8 Hz); ^{19}F-NMR: δ -63

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5 Selective oxidation of aromatic hydrocarbons to quinones

5.1 Introduction

As already mentioned in the previous chapters, the controlled oxidation of organic molecules is still a challenging task. Often, partially oxidized species are much easier to oxidize than the corresponding precursor molecules. This requires a well directed selection of the oxidizing agents as well as a strict control of reaction conditions.

However, the economic benefit of a selective and high yield oxidation reaction will for sure justify such efforts.

The oxidation of arenes can be considered as a typical example for the statements made above. Different intermediates with different stabilities against overoxidation can be obtained more or less selectively by application of the appropriate oxidizing agents.

The selective oxidation of arenes offers an efficient access to substituted 1,4-quinones.

The most important industrial process for the production of 1,4-quinones, such as 1,4-naphthoquinone or 2-methylnaphthoquinone (menadione), are based on the selective oxidation of corresponding naphthalenes with air or oxigen at 250 – 450 °C and 1 – 10 bar, over a catalyst containing vanadium pentoxide [1], or can alternatively be obtained in liquid phase by using stoichiometric amounts of chromium trioxide or cerium(IV) compounds in sulphuric acid [2].

Obviously these processes do not meet the standard of today's environentally requirements and are becoming impracticable.

1,4-naphthoquinone is industrially significant as an intermediate in the anthraquinone synthesis by Kawasaki or Bayer methodology [3-4].

1,4-naphthoquinone has been described as a polymerization regulator [5] and as a hardener for photochemically cross-linked polyesters [6]. It is used as a corrosion inhibitor and as a stabilizer for transformer oils. It reacts with cyclic aryl phosphinic acid esters to give 1,4-naphthalene diol adducts, which can be used for the production of thermally stable, flame-resistant polyesters [7-9]. Quinones take also part in many biological processes due to their versatile redox chemistry [10].

Beside their involvement in photosynthesis and the respiratory chain, quinone based vitamins are important food additives, e.g. menadione (vitamin K_3) and 2,3,5-trimethylbenzoquinone, a crucial intermediate for vitamin E [11-12].

This application has implicated intense investigations on the evaluation of new synthetic methods for the production of these compounds. Most routes start from versatile substituted naphthalene or polycyclic aromatic substrates and thus include at least one oxidation step.

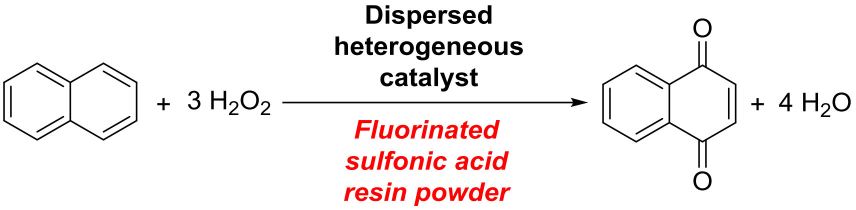
They can be divided into three groups:

1) Reactions wherein a metal derivative is used as a stoichiometric oxidizing agent. This is mainly performed with chromium(VI), or with cerium(IV). Both oxidizing agents can either be used directly or generated *in situ*, for example by anodic oxidation of low valent Cr^{III} o Ce^{III} precursors. From an economic point of view such procedures have become impracticable.
2) Reactions wherein a metal derivative is used as a catalyst in combination with hydrogen peroxide as the oxygen source. In some cases percarboxylic acids or oxygen gas can be employed instead of H_2O_2. A whole series of transition metal complexes have shown catalytic activity for the oxidation of arenes to quinones: ruthenium [13], vanadium [14], chromium [15], molybdenum and tungsten [16], rhenium [17], palladium [18], cerium [19], phthalocyanine [20] or porphyrine [21] complexes and zeolites [22].

Depending on the catalyst used, these routes are obviously more environmentally benign then those discussed above.

3) Oxidation without any metal catalyst. Such reactions have only rarely been reported. The oxidation of condensed aromatic compounds in the presence of acetic acid was first described in 1940 [23]. Other combinations of carboxylic/percarboxylic acids have also been reported [24].

We present here an improvement of the latter system wich opens up an efficient access to large examples of quinones by Brønsted acid activation of hydrogen peroxide resulting in products which are not contaminated by traces of metal catalysts.

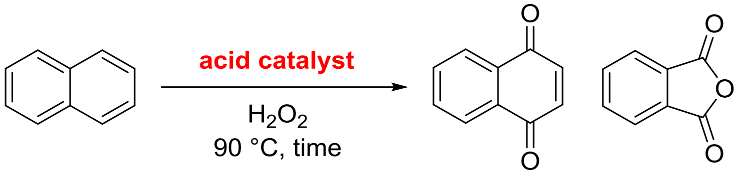


5.2 Results and discussion

Firstly, the model reaction of naphthalene oxidation was studied investigating different catalysts and conditions. In a typical experiment, 2 mmol of naphthalene were warmed at 90 °C with 35% aqueous solution of H_2O_2 in presence of 250 mg of solid catalyst using glacial acetic acid as solvent, for 24 hour.

Upon cooling, the solid was filtered and the resulting homogeneous solution was poured onto a mixture of 50 ml of diethyl ether and 50 ml of cold water and the crude product was extracted into the organic phase. A sample of this phase was directly subjected to GC analysis to determine conversion and yield. The results obtained are shown in **Table 1**.

Table 1. Catalytic activity of various acid catalysts



1a **2a** **3a**

Entry	Catalyst	Conv. 1a (%)[a]	Sel. 2a (%)[a]
1	-	8	13
2	H_2SO_4	82	90
3	$-(CH_2)_3-SO_3H@SiO_2$	61	55
4	Aquivion@NP-SiO_2	69	68
5	SiO_2	10	5
6	Aquivion PW66S	77	81

Reaction conditions: naphthalene (2 mmol), 35% aqueous H_2O_2 (0.524 μl, 6 mmol), acid catalyst (5 mol% for homogeneous acids, 200 mg for solid ones), at 90 °C for 24 hours; [a] by GC.

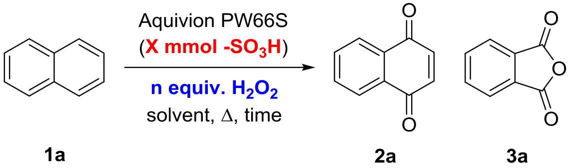
Aquivion powder PW66S resulted to be a better catalyst than Aquivion supported samples (entry 3-4), leading to better conversion (77%) and selectivity (81%).

Results obtained with Aquivion powder were similar to those obtained performing the reaction with the more harmful and less eco-friendly sulphuric acid. The reaction without catalyst or with silica (entry 1 and 5) were not so good for the production of 1,4-naphthoquinone (respectively 8 and 10% of conversion and only 13 and 5% of selectivity). In these cases the major product was phthalic anhydride.

After these interesting preliminary results, we decided to try to further optimize parameters such as reaction temperature, quantity of catalyst, reagent molar ratio, solvent, choosing Aquivion PW66S as model catalyst.

Several results obtained are shown in **Table 2**.

Table 2. Catalytic activity of Aquivion PW66S under different conditions.



Entry	T °C	Cat. (-SO$_3$H mol %)	H$_2$O$_2$ / 1a	Solvent	Conv. 1a (%)[a]	Sel. 2a (%)[a]
1	80	13 mol %	3:1	acetic acid	53	94
2	90	13 mol %	3:1	acetic acid	77	81
3	100	13 mol %	3:1	acetic acid	83	63
4	80	7 mol %	3:1	acetic acid	51	96
5	80	1.5 mol %	3:1	acetic acid	47	98
6	80	1.5 mol %	6:1	acetic acid	91	95
7	80	1.5 mol %	10:1	acetic acid	99	46
8 [b]	80	1.5 mol %	6:1	hexane	-	-
9 [b]	80	1.5 mol %	6:1	ethanol	6	94
10 [b]	80	1.5 mol %	6:1	acetonitrile	68	97

Reaction conditions: naphthalene (2 mmol), 5ml of solvent, for 24 hours; [a] by GC; [b] CH$_3$COOH/co-solvent ratio: 1.5:1

The first parameter optimized was the reaction temperature, in order to determine the best temperature to obtain the maximum conversion together with a good selectivity.

The model reaction was carried out at different temperatures, starting from 80 to 100 °C and using a 1:3 molar ratio naphthalene/hydrogen peroxide, 5 ml of acetic acid as solvent and 200 mg of catalyst, keeping the temperature constant for 24 hours.

Data in table 2 show that at 80 °C the conversion is not so good (53%) but it is possible to obtain **2a** with a selectivity of 94% (entry 1).

Increasing the temperature to 90 °C (entry 2) conversion grow up to 77% while maintaining a good level of selectivity (81%).

On the contrary, conducting the reaction at 100 °C, a further increase in conversion (83%) was registered together with a lower selectivity that decreased to 63% (entry 3).

These founding suggested that the best temperature was 80°C.

Therefore, the model reaction was conducted at 80 °C using decreasing amounts of catalyst. From the data reported in the table 2, we can conclude that reducing the catalyst amount could led to an improvement in selectivity even maintaining the conversion unaltered (entry 4-5).

The amount of the oxidizing agent was also examined in order to improve the yield and selectivity of the reaction. Besides the exact stoichiometric molar ratio between hydrogen peroxide and substrate (3:1), various reactions with excess of oxidant were carried out.

With a molar ratio of 6:1 (entry 6), the conversion improves up to 91%, and the selectivity is very good (95%), while in entry 7, with a larger excess of H_2O_2, a quantitative conversion (99%) was registered, together with a lower selectivity due to the formation of higher amount of phthalic anhydride and phthalic acid.

After that the role of solvent was also investigated. First of all, the reaction in absence of acetic acid does not proceed.

Therefore, co-solvents employed in this study, in addition to acetic acid, were hexane, dichloromethane, water, acetonitrile, ethyl acetate, ethanol, DMF and water (5 ml of acetic acid, 7.5 ml of co-solvent).

In table 2 are show only few of obtained results, but is clear that only the use of glacial acetic acid afforded the best results concerning conversion and selectivity (entry 8-10).

Then some experiments were performed in order to determine the optimum amount of acetic acid.

Employing 2 ml of glacial acetic acid for 2 mmol of naphthalene, the reaction gives the same results than the model reaction conducted with 5 ml of carboxylic acid.

On the contrary, by carrying out the reaction with a lower amount of solvent the conversion of naphthalene decreased.

Under the best reaction conditions identified in the previous steps, we analysed the progress of reaction over time (**Figure 1**).

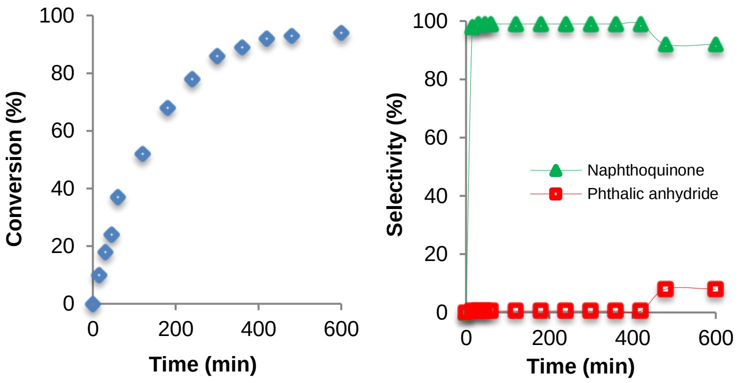


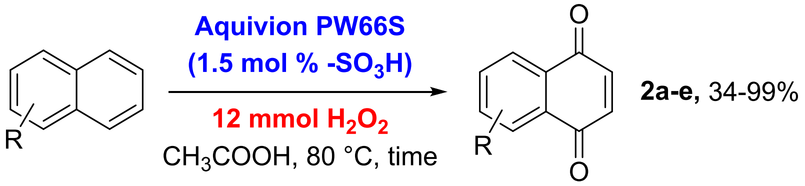
Figure 1. 1a conversion and selectivity in function time

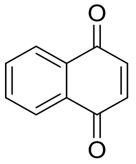
Conversion increases during the first 5 hours, and then it reaches a plateau near 95%.

At the same time the selectivity to 1,4-naphthoquinone is very high, around 100%, during the first 7 hours, and then its value decreases to 92% due to the formation of little amounts of phthalic anhydride.

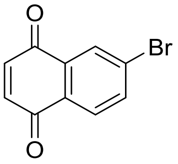
So, with best conditions in our hands, we then studied the scope of this reaction.

Firstly we tested some substituted naphthalenes (**Table 3**).

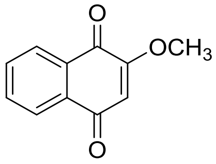




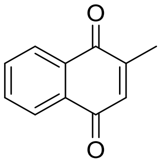
2a, 87% (95%)



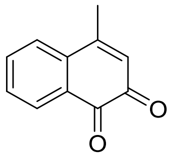
2b, 34% (100%)



2c, 94% (94%)



2d, 99% (99%)



2e, 46% (71%)

Reaction scope, conditions as Table 2, entry 6; isolated yields and selectivity into the brackets.

In case of substituted naphthalenes, the ring where the quinone moiety is formed depends on the electron donor/acceptor characteristic of the substituent.

On one side, with a substituent like bromine or other halogens (entry 2b), the quinone is formed on the unsubstituted ring because bromine stabilizes the second ring and makes it less reactive than the first one.

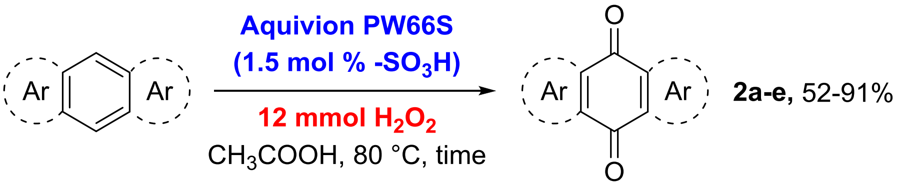
On the other hand, if $-OCH_3$ or $-CH_3$ are the substituents at the same position (entry 2c-d), the quinone is formed on the substituted ring instead, as the resonant structures that the $-OCH_3$ and $-CH_3$ enable make it more reactive than the first one.

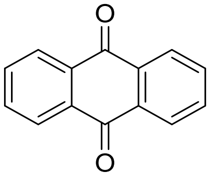
Testing 1-methylnaphthalene (entry 2e), the main product was the corresponding 4-methyl-1,2-naphthoquinone, but the yield and the selectivity found were lower compared to other cases (46 and 71% respectively).

Trying 1-bromonaphthalene and 1-methoxynaphthalene, carrying substituents that could act as leaving groups, the only isolated product was 1,4-naphthoquinone with very good yield and selectivity.

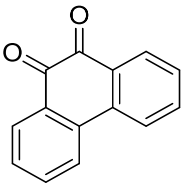
These preliminary results suggest that the reaction is completely regioselective on the most activated ring.

Subsequently, we tried some polycyclic aromatic compounds under the same reaction conditions (**Table 4**).

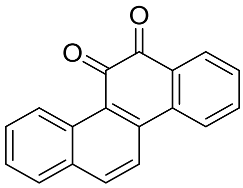




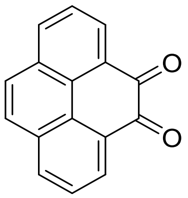
2f, 89% **(94%)**



2g, 91% **(90%)**



2h, 62% **(85%)**



2i, 52% **(87%)**

Reaction scope, conditions as Table 2, entry 6; isolated yields and selectivity into the brackets.

The four conducted experiments (entry 2f-i), showed that the middle ring of substrates is the reacting ring.

This ring is the most reactive in according to Clar's rule [25-26]. For example, in case of phenanthrene (entry 2g) the most important Clar structure has two isolated and localized p-sextets at the extremities, therefore in this molecule the outer rings have greater aromatic character whereas the central ring is less aromatic and then chemically more reactive.

For the entry 2h-i, some solubility problems occurred with the starting materials and the oxidative solution. To overcome this problem an appropriate co-solvent (MeCN, 5ml) was added to ensure a perfect homogeneity of the reaction.

However, for these particular types of complex substrates, the reaction showed to be slightly less selective.

At the beginning of reaction, before the hydrogen peroxide addition, it was possible to notice that the solid catalyst was effectively dispersed in the acetic acid used as solvent, giving a homogeneous solution.

After the reaction and the work-up the solid catalyst can be recovered easily since it precipitates in the extracted aqueous phase.

Its identity was proven by a FT-IR comparison of fresh material with recovered material (**Figure 2a-b**).

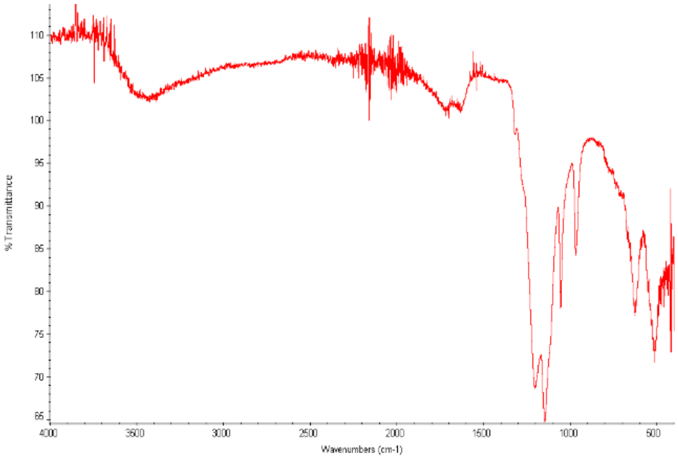


Figure 2a. Fresh Aquivion powder

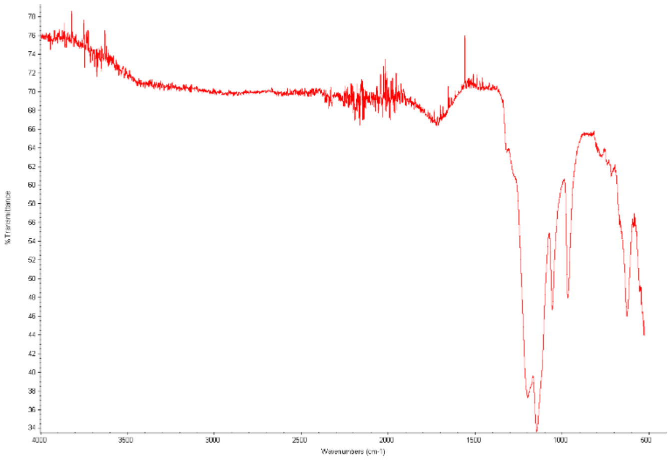


Figure 2b. Recovered Aquivion powder

During the reaction, we did not detect any intermediate of naphthalene oxidation, so we performed further experiments to get insights on the reaction mechanism (**Figure 3**).

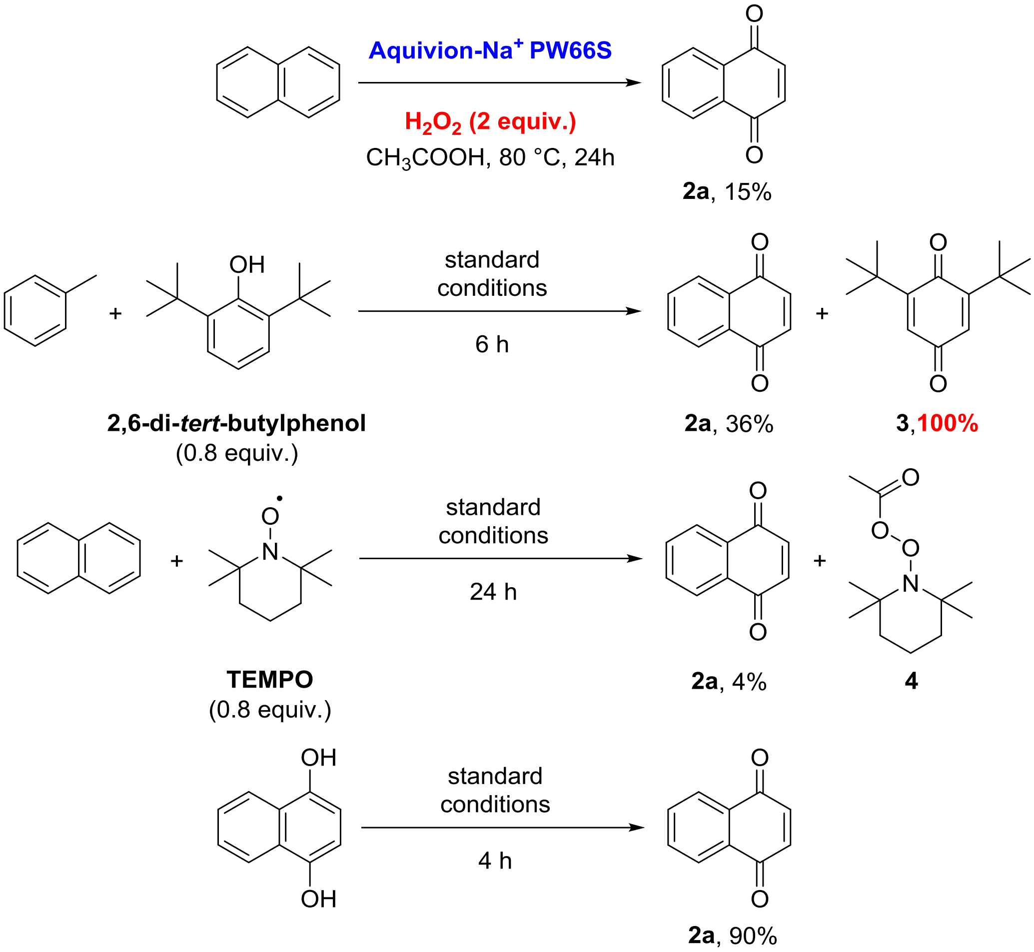


Figure 3. Mechanism probes

To ascertain that sulphonic acid groups act as catalyst at the molecular level in analogy with former oxidation reaction (**Chapter 3**) and homogeneous sulphuric acid (**Table 1**), we treated our material with an excess of aqueous NaOH. The resulting solid did not exhibit anymore protic acid sites, as determined by titration. It proved to be inactive and unable to induce a deep formation of **2a** too (**Figure 3**).

Usually, the oxidation reactions involving transition metals as catalysts occur radically. In our case, there are no transition metals, but the hypothesis that the reaction could take place through a radical mechanism has been evaluated.

To check this hypothesis the model reaction was carried out in the presence of 2,6-di-*tert*-butylphenol, known for its radical inhibitory properties.

2,6-di-*tert*-butylphenol reacts with the radical species eventually formed during the process affording an oxygen radical that due to the presence of the two *tert*-butyl groups is a stable radical (persistent radical).

After 6 hours we noticed that the starting 2,6-di-*tert*-butylphenol was completely converted to 2,6-di-*tert*-butyl-1,4-benzoquinone and only 36% of 1,4-naphthoquinone was obtained.

This interesting result may indicate that the reaction follows a radical mechanism, but could also open up to a new alternative synthetic way to obtain 1,4-benzoquinones from more or less activated phenols.

A second test to support the radical hypothesis was also performed: the model reaction was carried out in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), another radical inhibitor.

Analysis of the crude reaction by NMR showed how the reaction was dramatically inhibited by the presence of TEMPO: only 4% of 1,4-naphthoquinone was detected.

We were instead able to identify a recombination product **4** (92%, **Figure 4a-b**).

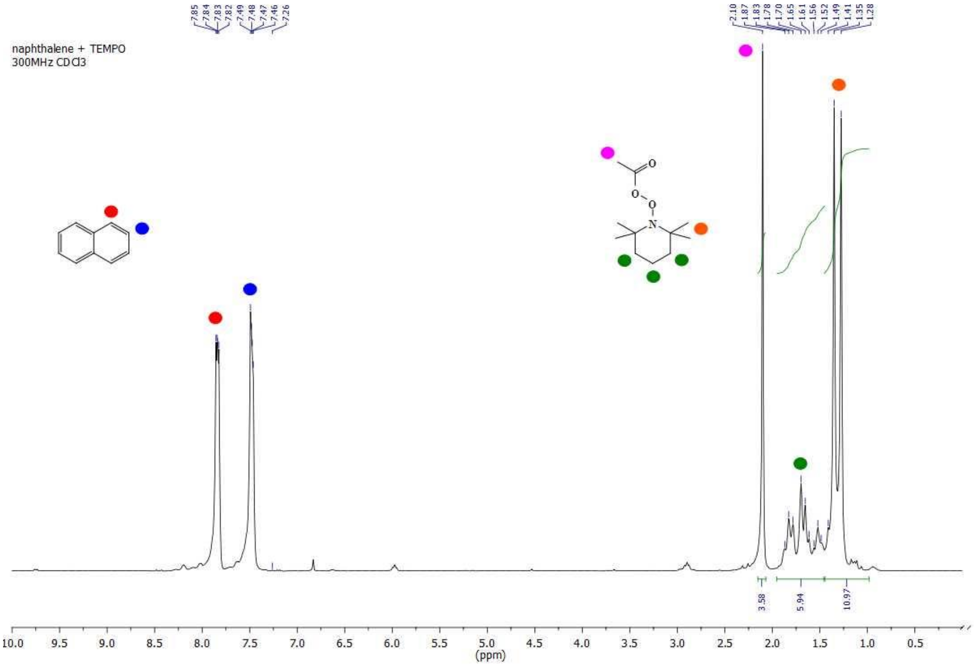


Figure 4a. ^{1}H-NMR spectra of recombination product **4**.

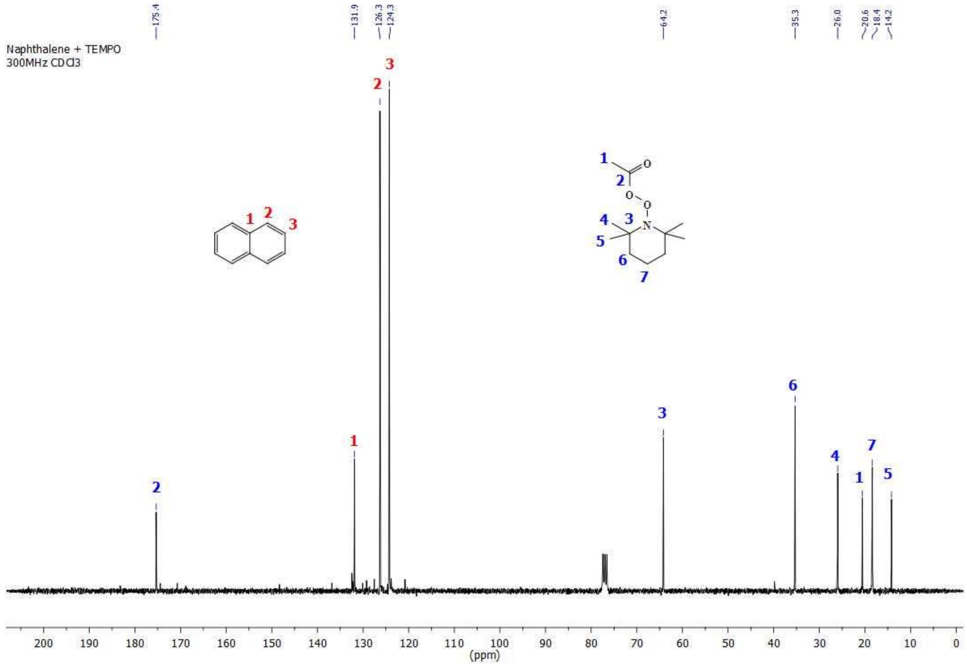


Figure 4b. ^{13}C-NMR spectra of recombination product **4**.

The identification of adduct **4** allowed us to understand that the presence of Aquivion in the reaction environment ensures the peracetic acid formation, because its synthesis requires the presence of a strong acid [27-29].

A further clue of reaction mechanism was provided by the 1,4-dihydroxynaphthalene oxidation under same reaction conditions. The entire starting substrate was completely converted into 1,4-naphthoquinone with a yield of 90% after just 4 hours.

On the basis of these results we can conclude that the reaction follows a radical mechanism and that probably occurs through a hydroxylated intermediate.

On the basis of the aforementioned observations, we propose the plausible reaction mechanism depicted in **Figure 5**.

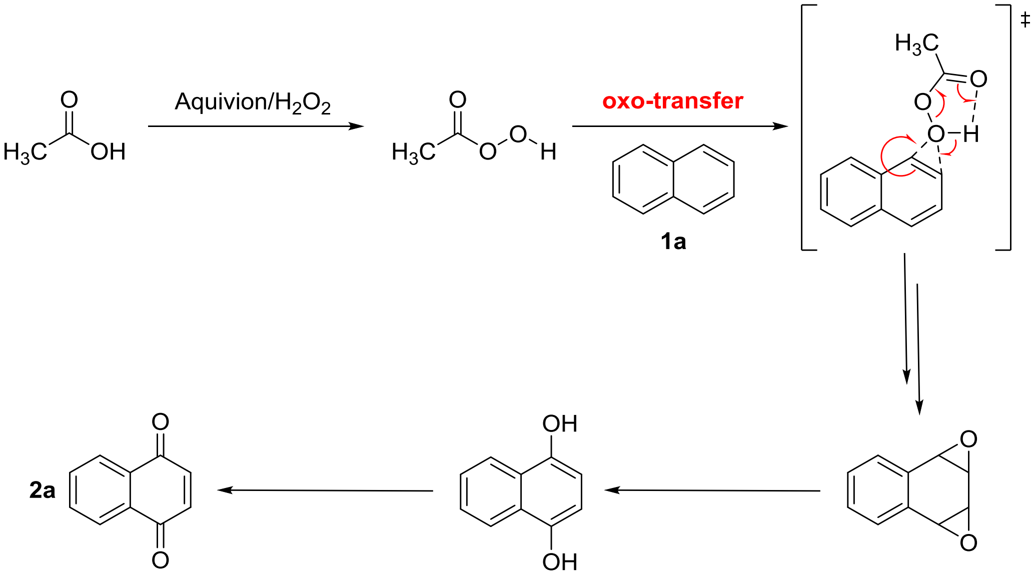


Figure 5. Possible reaction rationale

The possible mechanistic route for the oxidative conversion of **1a** to **2a** starts with the strong perfluorosulphonic acid resin that gives the right *pK*$_a$ value for the *in situ* synthesis of peracetic acid [30].

The oxidation proceeds *via* a two-fold epoxidation with subsequent reorganization to 2-methyl-1,4-naphthoquinone, which then should rapidly be further oxidized to **2a** [31-32].

5.3 Conclusion

In conclusion, we have optimized a naphthalene oxidation processes to 1,4-naphthoquinone, using methods in accordance with some of the principles of green chemistry.

The best catalyst utilised to promote this synthesis the Aquivion powder, a perfluorinated resin-sulphonic acid. It is a heterogeneous "metal-free" catalyst whose active catalytic sites are the acid sulphonic groups. This catalyst (22 mg, 1.5 mol %) in presence of 2 mmol of naphthalene, 12 mmol of hydrogen peroxide, 5 mL of acetic acid, 80 ºC, 5 h, resulted to be effective and selective, affording the product in 87% yield and 95% selectivity.

5.4 Experimental section

The catalytic oxidation reaction was performed at atmospheric pressure in a two necked round bottom flask, equipped with magnetic stirrer, condenser and plug. For a typical experiment, 22 mg of Aquivion PW66S powder was weight and dispersed in 5 ml of glacial acetic acid.

It was bring at 80 °C for a few minutes under vigorous stirring, then 2 mmol of substrates was added and left under stirring until complete dissolution.

At this point, 1.05 ml of 35% hydrogen peroxide (12 mmol of H_2O_2) was added dropwise. The reaction was stirred at 80 °C until complete conversion of substrate, then it was poured onto a mixture of 100 ml of H_2O cold water and 50 ml of ethyl ether and the organic phase was extracted into organic phase. Aqueous phase was extracted again with other 2X50 ml of ethyl ether.

The organic phases were combined with the first and washed with 50 ml of brine. The ethyl ether solution was dried over $NaSO_4$ and the solvent was removed under vacuum. The desired product was purified by flash column chromatography on silica gel and identified by NMR spectroscopy.

Characterization of products

(2a)
^{1}H-NMR: δ 8.08 (dd, J = 5.7, 3.3 Hz, 2H), 7.76 (dd, J = 5.7, 3.4 Hz, 2H), 6.98 (s, 2H); ^{13}C-NMR: δ 185.0, 138.6, 133.9, 131.9, 126.4

(2b)
^{1}H-NMR: δ 8.21 (d, J = 1.8 Hz, 1H), 7.91 (dt, J = 5.1, 8.3 Hz, 2H), 6.99 (s, 2H); ^{13}C-NMR: δ 184.2, 183.8, 138.8, 138.4, 137.0, 132.9, 129.5, 128.2

(2c)
^{1}H-NMR: δ 8.03-7.96 (m, 2H), 7.69-7.60 (m, 2H), 6.10 (s, 1H), 3.84 (s, 3H); ^{13}C-NMR: δ 184.7, 180.0, 160.3, 134.3, 133.3, 131.9, 131.0, 126.6, 126.1, 109.8, 56.4

(2d)
^{1}H-NMR: δ 8.04 (ddd, J = 3.2, 5.8, 11.5 Hz, 2H), 7.69 (dd, J = 3.3, 5.7 Hz, 2H), 6.81 (s, 1H), 2.17 (s, 3H); ^{13}C-NMR: δ 185.4, 184.9, 148.1, 135.6, 133.5, 132.1, 126.4, 126.0, 16.4

(2e)
^{1}H-NMR: δ 7.99 (dd, J = 4.3, 8.4 Hz, 1H), 7.84-7.70 (m, 1H), 7.63-7.46 (m, 2H), 6.90 (s, 1H), 2.75 (s, 3H); ^{13}C-NMR: δ 187.0, 185.4, 141.3, 140.4, 137.9, 136.9, 133.3, 130.0, 125.3, 22.6

(2f)
^{1}H-NMR: δ 8.31 (m, 4H), 7.80 (m, 4H); ^{13}C-NMR: δ 183.1, 134.1, 133.5, 127.2

(2g)
^{1}H-NMR: δ 8.17 (dd, J = 7.9, 1.3 Hz, 2H), 8.00 (d, J = 7.9 Hz, 2H), 7.70 (td, J = 7.4, 13 Hz, 2H), 7.45 (t, J = 7.9 Hz, 2H); ^{13}C-NMR: δ 180.3, 136.0, 135.8, 131.0, 130.5, 129.6, 124.0

(2h)

^{1}H-NMR: δ 9.43 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.6 Hz, 1H), 8.18 (d, J = 7.4 Hz, 1H), 8.12 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 7.9 Hz, 1H), 7.77 (t, J = 8.1 Hz, 1H), 7.74 (t, J = 8.5 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H; ^{13}C-NMR: δ 184.6, 182.5, 138.3, 137.8, 137.1, 136.5, 134.2, 132.7, 131.3, 131.1, 130.4, 130.3, 129.1, 128.1, 127.6, 126.3, 125.6, 121.5

(2i)

^{1}H-NMR: δ 8.18 (d, J = 6.8 Hz, 2H), 7.95 (d, J = 7.4 Hz, 2H), 7.61 (s, 2H), 7.52 (t, J = 6.8 Hz, 2H); ^{13}C-NMR: δ 180.5, 136.0, 132.2, 130.2, 130.1, 128.4, 128.2, 127.5

(3)

^{1}H-NMR: δ 6.67 (s, 2H), 1.24 (s, 18H); ^{13}C-NMR: δ 188.9, 187.6, 157.7, 129.9, 35.4, 29.2

(4)

^{1}H-NMR: δ 2.10 (s, 3H), 1.87-1.49 (m, 6H), 1.31 (d, J = 22.19 Hz, 12H); ^{13}C-NMR: δ 175.4, 62.2, 35.3, 26.0, 20.6, 18.4. 14.2

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6 Oxidative desulphurization of DBT with H_2O_2 catalyzed by TiO_2 on silica

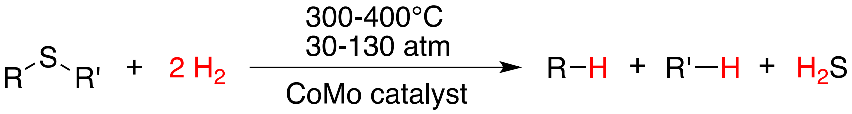
6.1 Introduction

The oil industry is facing increasing pressure to remove organic sulphur compounds from transportation fuels. Liquid fuels contain a large variety of sulphur compounds (thiols, sulphides, disulphides and thiophenes), which generate SO_x and airborne particulate emissions during combustion. This contributes not only to acid rain, but also to poison catalytic converters for the treatment of exhaust emission.

The sulphur level in diesel fuels in EU is limited to 10 ppm [1].

Several process have been proposed in the past to deal with the problem of removing the sulphur from light oil.

The most important and common industrial process, called hydrodesulphurization (HDS), consists in treating the fuel under high temperatures and high pressures with hydrogen. HDS is a process in which light oil is heated, mixed with hydrogen and fed to a reactor packed with a cobalt and molybdenum pelleted catalyst. Temperatures in the reactor typically range from 300 to 380 °C and pressure range from as low as 15 to as high as 90 bars depending on the difficulty of removing the sulphur [2].



Scheme 1. Simplified reactions in HDS process

Currently HDS technology is able to desulphurize aliphatic and acyclic sulphur-containing compounds quite efficiently. However, this process is limited when treating dibenzothiophene (DBT), especially in the case of DBTs having alkyl substituents at position 4 and/or 6 [3]. Thus, the production of ultra-clean light oil inevitably requires severe operation conditions and, especially, highly active catalysts.

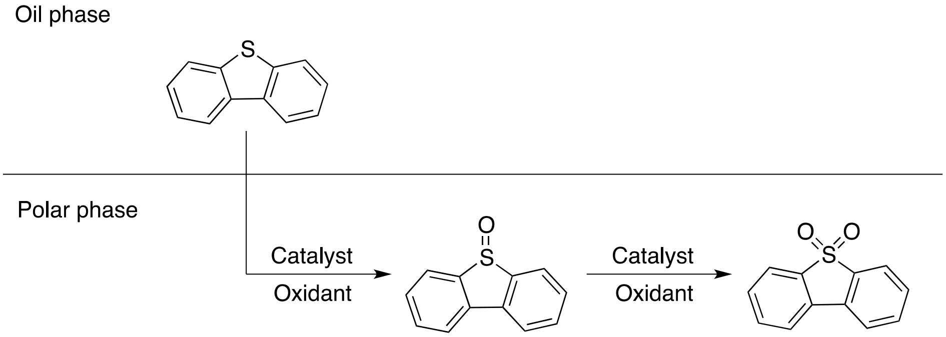
An alternative process that can be carried out under moderate conditions and without requirements of H_2 and is required.

One of the new processes developed in recent years is the oxidative desulphurization (ODS). The greatest advantage of ODS as compared with the conventional HDS processes is that it can be carried out in liquid phase under very mild conditions as (near) room temperature and under atmospheric pressure. In ODS reactions, the divalent sulphur can be oxidized by the electrophilic addition reaction of oxygen atoms to form the hexavalent sulphur of sulphones.

Indeed another feature of ODS is that the refractory S-containing compounds can be easily converted by oxidation.

This desulphurization process includes two stages: (i) oxidation in a first step; and (ii) liquid extraction at the end.

Sulphur-containing compounds are oxidized using a selective oxidant to form compounds that can be preferentially extracted from light oil due to their increased relative polarity. Many types of oxidants have been used such as nitrogen oxides, nitric acid, hydrogen peroxide, ozone, t-BuOOH, oxygen, air and peracids [4].



Scheme 2. Schematic biphasic ODS reaction

The extraction solvent is a non-miscible solvent with light oil and it must be selective for the relative polar oxidized S-containing compounds. Acetonitrile is an adequate solvent considering that it has a relatively low boiling point (82 °C) and it can be easily separated from the sulphones by distillation.

Peracids, produced in situ by reaction between hydrogen peroxide and carboxylic acid for safety reason, are very powerful oxidizing agents and are able to oxidize sulphur compounds. However the use of a catalyst is necessary. The most common option is the use of transition metal salts, i.e. tungsten [5], cobalt [6] or iron [7] salts.

A second family of oxidants that has been studied is based on the use of organic hydroperoxides. The most widely employed hydroperoxide is t butylhydroperoxide (TBHP). An ODS process based on this oxidant was patented by Lyondell Chemicals [8] and EniChem/UOP [9].

The oxidation of sulphur compounds with organic hydroperoxides occurs in the presence of a catalysts. The active center of these catalysts is a transition metal in a high oxidation state with Lewis acidity, such as Mo(IV) [10], Ti(IV), V(V), W(IV), etc.

The best results were obtained with titanium catalysts and their silylation improves their activity and longevity [11].

Currently the better oxidizing method is represented by hydrogen peroxide in presence of proper catalyst. The first papers on ODS with hydrogen peroxide are related to the use of a photosensitizer like benzophenone [12].

The second group of catalysts is based on transition metal salts in a high oxidation state with Lewis acidity [13].

The main problem of this system is related to the presence of two reaction phases: an oil phase with the sulphur compounds and a polar phase that contains the oxidant (H_2O_2), which is not soluble in the oil phase. For this reason, some authors have studied the use of phase transfer catalysts [14].

The ideal systems use heterogeneous catalysts. Over the last few years selective oxidation of sulphur-containing compounds by H_2O_2 has been carried out using a large number of solid redox catalyst: Ti [15], V [16], W [17], Mo [18], Co/Mn [19], Ag [20], Au [21], Re [22].

In previous studies conducted in our group, we have found out that sulphonic resin Amberlyst 15 is able to oxidize organic sulphides with diluted hydrogen peroxide solutions, in continuous flow conditions [23].

Therefore, we were interested in testing our catalysts based on perfluorinated sulphonic acid resin in the ODS of fuels with this oxidant. In this chapter preliminary results in the oxidation of a model compound dibenzothiophene (DBT) with ultra-diluted aqueous H_2O_2 (3%) are reported. I was able to test a wide range of different types of catalysts.

6.2 Results and discussion

As mentioned in the previous paragraph, our investigation began with the variation of different reaction parameters, using Amberlyst 15 as model catalyst.

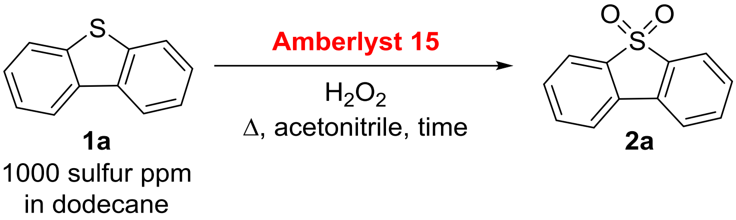
The catalytic oxidation reactions were performed at atmospheric pressure in a glass batch reactor. The reactor was immersed in an oil bath to keep the reaction temperature constant. A magnetic stirrer was used to blend the reaction mixture. In a typical experiment, a proper amount of catalyst was suspended under stirring (800 rpm) in 2 ml of model fuel solution (1000 ppm of sulphur in dodecane). The adequate volume of hydrogen peroxide (3wt% aqueous solution) in 2 ml of acetonitrile was added at the beginning of the experiment.

Blank run was carried out by mixing the reactants in the absence of catalyst. Samples of polar and apolar phase were withdrawn periodically and analyzed on an Agilent Technology 1260 Infinity HPLC equipped with a C_{18}

column, using MeCN/H2O 70:30 as eluent, with a flow rate of 1 ml/min and with a UV-Vis detector (255 nm).

The preliminary results obtained are shown in **Table 1**.

Table 1. Batch optimization of DBT oxidation with 3% aqueous hydrogen peroxide



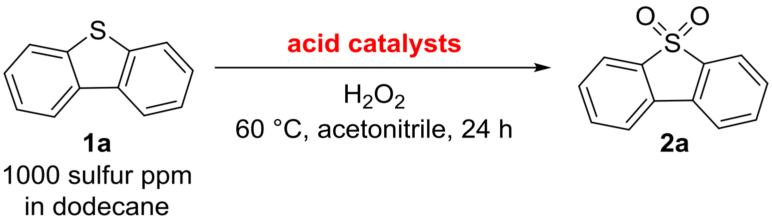
Entry	H_2O_2/1a	T °C	Cat. mg	Final sulphur (ppm) [a]
1	5:1	60	50	810
2	10:1	60	50	698
3	20:1	60	50	673
4	10:1	80	50	650
5	10:1	60	250	345

Reaction conditions: 2 ml of DBT solution 1a in dodecane (0.024 mol/L), 2 ml of acetonitrile, catalyst: Amberlyst IR120 H, X ml of H_2O_2 solution at 3 wt%, time: 24h; [a] by GC

Considering the discouraging results obtained from these tests (final Sulphur content >> 10 ppm) we decided to try a wide range of materials with different acid properties (Lewis or Brönsted), which can activate a so diluted hydrogen peroxide solution, under the reaction conditions obtained so far.

Several results obtained are shown in **Table 2**.

Table 2. Catalysts screening



Entry	Catalyst	1a Conversion % [a]	Final sulphur (ppm) [a]
1	-	4	946
2	Nafion NR50	20	459
3	Aquivion PW66S	35	464
4	Aquivion@NP-SiO_2	46	423
5	Kieselgel 60 Å	3	952
6	H-BEA 150	32	460
7	Al_2O_3 S-A	65	201
8	α-Fe_2O_3	30	470
9	TiO_2 anatase	49	242
10	TiO_2 rutile	27	445
11	Ti-SBA15	26	355
12	TS-1	64	263
13	TiBSi	68	231
14	TiO_2@SiO_2	98	8

Reaction conditions: 2 ml of DBT solution 1a in dodecane (0.024 mol/L), 2 ml of acetonitrile, catalyst: 250 mg, 0.533 ml of H_2O_2 solution at 3 wt%, time: 24h; [a] by GC

Without catalyst the reaction does not really work (entry 1). Testing other materials belonging to perfluorinated sulphonic acid family there was no really improvement in final sulphur ppm content (entry 2-3), compared to the results obtained with Amberlyst. Similar results were achieved utilizing the supported Aquivion material (entry 4).

It is reported in the literature that the oxidation of DBTs with hydrogen peroxide is possible over other various catalytic heterogeneous systems, such as zeolites [24], metals oxide [25] or titanium silicalites [26]; mesoporous iron oxide (entry 8) was too little active.

In general, when tetravalent cations like Ti^{4+}, Zr^{4+}, V^{4+}, Sn^{4+}, etc. are incorporated into the framework of silica or other inorganic supports, the electro-neutrality is maintained and some particular redox properties are acquired on the support surface [27].

Typical catalytic supports, such as H-BEA zeolite, silica, titanium oxide and alumina, exhibit low ODS activity of DBT. The slightly better result obtained with alumina (entry 7) is probably due to its better adsorptive properties towards DBT and its sulphone.

However, in view of recent studies, where Ti-containing catalysts showed good activity in the oxidation of different S-bearing compounds [28], we decided to try to prepare some titanium (3.5 wt%) based materials to tested in the ODS reaction.

The Ti-SBA15 (entry 11) material was prepared following similar procedures reported in literature [29-30], but showed worse results than those obtained with anatase. Probably because of a non-optimal dispersion/incorporation of titanium atoms into the mesoporous silica matrix.

TS-1 (entry 12), prepared following a procedure described in literature [31], proved to be active like anatase, probably according to the reduced size of the pores and channels, which restricted the access of the reagents to the active sites, allowing only superficially reaction.

Wondering that a material with an increased Lewis acidity could probably be more active, we planned to synthesize a titanium boralite, following some procedures reported in the literature (entry 13) [32].

Unfortunately, the reaction did not give the expected results. So, since that the anatase was shown to be rather active, we decided to prepare a material that exhibited the most finely dispersed anatase particles on an inert support such as commercial silica [33].

The XRD analysis of the prepared material, before and after calcination, confirms what was mentioned earlier (**Figure 1**).

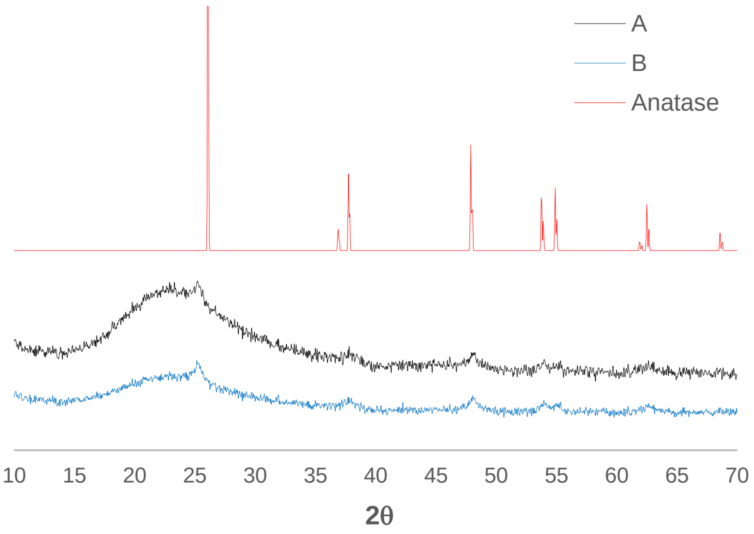


Figure 1. XRD pattern of TiO2@SiO2 synthesized samples: A) fresh catalyst, B) calcined catalyst

The peaks reported in the samples A and B show a similar pattern that pure anatase phase (red spectra) and their broadness indicate small size and amorphous morphology of the TiO_2 nanoparticles dispersed on the amorphous silica surface.

Finally, testing this material (entry 14) we found an almost total conversion of initial DBT present in the apolar solution, detecting only 8 ppm of residual sulphur only.

Under the best reaction conditions identified in the previous steps, we analysed the progress of reaction over time (**Figure 2**).

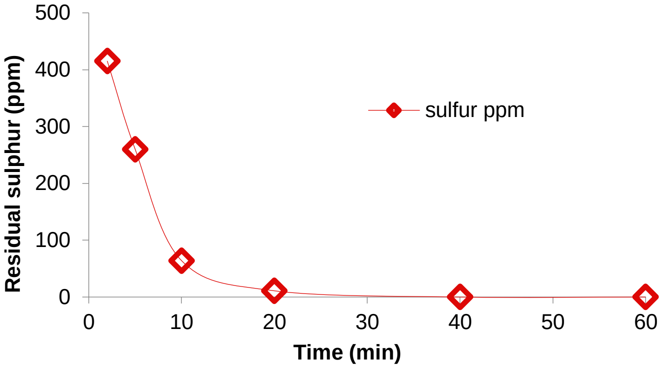
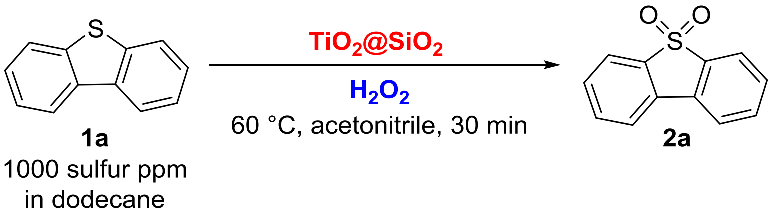


Figure 2. Reaction trend for batch oxidation of DBT under optimized conditions

Surprisingly, reaction with $TiO_2@SiO_2$ catalyst turned out to be particularly fast. Just after 20 minutes, residual sulphur was below the 10 ppm imposed by the new anti-pollution regulations.

Stated the excellent results obtained, stability and reusability of the catalysts were assessed recovering the solids acid by filtration on Büchner funnel at the end of the reaction, washing with 10 ml of acetonitrile, drying and repeating the oxidation test under the same conditions (**Table 3**).

Table 3. Recycling tests with H_2O_2 solution



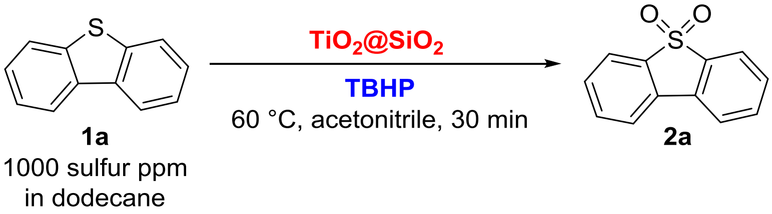
Entry	1a Conversion % [a]	Finale sulphur (ppm) [a]
1	99	5
2	42	234
3	35	404
4	31	424
5	31	425

Reaction conditions: 2 ml of DBT solution 1a in dodecane (0.024 mol/L), 2 ml of acetonitrile, catalyst: 250 mg, 0.533 ml of H_2O_2 solution at 3 wt%, time: 30 min; [a] by GC

Unfortunately, as can be seen from the results reported in the table, the catalyst showed a rapid partial deactivation, until reaching a plateau around 420 ppm of final sulphur.

Replacing the hydrogen peroxide solution with a considered quite green organic hydroperoxide, like a TBHP solution at 3% in hexane, the same catalytic activity of the material was detected but no deactivation problems were encountered, as can be seen in **Table 4.**

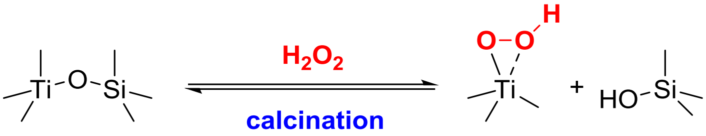
Table 4. Recycling tests with TBHP solution



Entry	1a Conversion % [a]	Finale sulphur (ppm) [a]
1	99	5
2	99	3
3	98	8
4	99	4
5	98	6

Reaction conditions: 2 ml of DBT solution 1a in dodecane (0.024 mol/L), 2 ml of acetonitrile, catalyst: 250 mg, 0.09 ml of $TBHP_2$ solution at 3 wt%, time: 30 min; [a] by GC

Probably, the reason for the rapid TiO_2@SiO_2 deactivation with hydrogen peroxide solution, is to bring again to the fact that the amorphous TiO_2-SiO_2 materials usually exhibited lower catalytic performance (in terms of activity, H_2O_2 efficiency and reusability) than the crystalline titanosilicates in the oxidation of organic substrates with aqueous solutions of H_2O_2 and thus their use was rather limited to oxidation reactions with dry organic hydroperoxides. This behavior has been ascribed to the much higher hydrophilicity of the amorphous materials leading to extensive water adsorption hindering the access to the Ti(IV) active sites [34-35] and also to the irreversible deactivation of these sites in the presence of aqueous H_2O_2 [36]. Indeed, the superior catalytic properties of crystalline titanosilicates can be related to their structural stability: the cleavage of the Si-O-Ti bonds by H_2O_2 [involved in the formation of the yellowish active peroxo sites from $Ti(OSi)_4$ sites] was reversible upon calcination (**Scheme 3**) [37].



Scheme 3. Formation of the Ti-peroxo sites

By contrast, in the case of amorphous Ti(IV)-grafted silica materials, like that prepared in our laboratory, the exposure to particularly diluted aqueous H_2O_2 led to the irreversible cleavage of Si-O-Ti bonds, while the cleavage of Si-O-Ti bonds was reversible after exposure to dry *tert*-butyl hydroperoxide in decane and calcination [36].

6.3 Conclusion

These preliminary results demonstrate that the desulfurization of DBT to the corresponding sulphone in hydrocarbon solution with diluted hydrogen peroxide solution can be effectively accomplished with titanium heterogeneous catalyst under mild reaction conditions.

This catalyst was easily prepared from commercial amorphous silica by grafting the titanium sites by reaction with $TiCl_4$.

The use of acetonitrile solvent proved to be highly effective for the ODS reaction. This enhancement in the reaction rate can be explained due not only to the higher solubility of the sulphone in acetonitrile, which facilitate its removal from the apolar phase, but also to the lower surface tension of liquid acetonitrile, which facilitates the transfer of product and reagent at the polar-apolar interface.

Unfortunately the catalyst showed a rapid partial deactivation in presence of water, and consequently not o good results were achieved when performing the same oxidation reaction with aqueous hydrogen peroxide.

Studies are under way to improve the material recyclability, modifying its hydrophobicity, to ensure a lower interaction between the surface and the water molecules present in the reaction environment.

6.4 Experimental section

General procedure for the synthesis of Ti-SBA15

10 g of surfactant P-123 (1.7 mmol) were introduced in a 500 ml three necked flask, equipped with a gas valve, drop funnel and bubble counter. 80 ml of a solution 1: 1 H2O/EtOH were added and reaction mixture was warmed at 35°C under argon atmosphere.

100 ml of a 2M HCl solution were then added.

18.4 ml of TEOS (83 mmol) and 0.4 ml of $TiCl_4$ (3.3 mmol, equivalent to 3.5 w/w %) were subsequently drop slowly into the flask.

The solution was kept under stirring at 35 °C for 1 day.

The resulting "gel" was transferred in a Teflon vessel and left it aging without stirring at 50 °C for 4 days.

Powder obtained was filtered, washed with plenty H_2O, dried overnight in an oven at 50 °C and finally calcined at 450 °C for 6 h.

BET Area: 732 m^2/g

General procedure for the synthesis of TS-1

Solution A: 0.5 g of surfactant P-123 (0.09 mmol) were dissolved in 1 ml of H_2O and 4 ml of TEOS and left under stirring for about 30 minutes to make it homogeneous.

Solution B: 0.07 ml of $TiCl_4$ (0.6 mmol) were dissolved in 3 ml of isopropanol and drip into solution A and the resulting solution was left under stirring for 12 h at room temperature, then raised the temperature to 80 °C maintaining stirring for another 3 h.

10 ml of H_2O was added and the solution was transferred into a crystallizer and allowed to dry at room temperature for 4 days.

Powder obtained was washed with copious amounts of H_2O and calcined at 500 °C for 6 h.

BET area: 412 m^2/g

General procedure for the synthesis of TiBSi

Solution A: 56 ml of H_2O, 5.1 ml of H_2O_2 at 30% and 1 ml of $TiCl_4$ (9.1 mmol) was united and left under vigorous stirring at room temperature for 2h.

Solution B: 50 ml of H_2O, 64.5 ml of TEOS (290 mmol) and 5 g of surfactant P-123 (0.86 mmol) to which was slowly added boric acid (58.2 mmol acid 3.6 g solution) dissolved in 120 ml of H_2O and it was left under vigorous stirring for 15 minutes.

Subsequently the solution B was brought at 65 °C and maintained for 3 h.

Left to cool to room temperature and drip the solution A into solution B and brought the pH to 11 with the addition of a concentrated solution of NH_3.

The resulting solution was transferred in a Teflon vessel and maintained at 175 °C for 5 days without stirring.

Powder obtained was filtered and washed with plenty H_2O, and calcined at 550 °C for 4 h.

BET area: 356 m^2/g

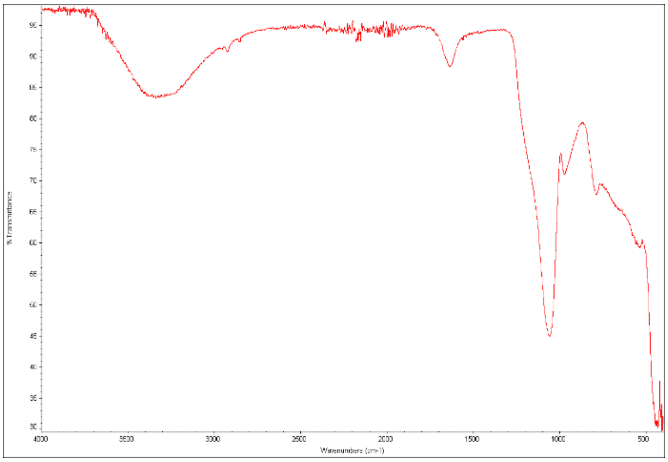
General procedure for the synthesis of TiO$_2$@SiO$_2$

10 g of dried commercial SiO$_2$ was put into a 50 ml three necked round bottom flask, equipped with gas valve, drop funnel and refrigerant provided with NaOH scrubber.

Argon atmosphere was created and 0.48 ml of TiCl$_4$ in 22 ml of heptane was slowly added through a dropping funnel. Raised the temperature to 100 °C and kept under stirring for 2 h. The cooler was removed and the temperature was raised to 130 °C and maintained until all the solvent is evaporated. Final powder was calcined at 450 ° C for 6 h.

BET area: 436 m^2/g

FT-IR:



The peak below 950 cm^{-1} is attributed to the combination of the stretching modes of the Si-O$^-$ species in Si-O-Ti^{4+} sequences involving tetrahedral coordinated Ti4+ ions [37].

The other peak below 800 cm^{-1} is due to the combination of the stretching modes of Si-O-Si and Ti-O-Ti. These features indicate the existence of Si-O-Ti binding between SiO_2 and TiO_2 species.

General procedure for the synthesis of **2a**

The catalytic oxidation reaction was performed at atmospheric pressure in a two necked round bottom glass reactor, equipped with magnetic stirrer, condenser and plug. For a typical experiment, 250 mg of catalyst was weight and suspended in 2 ml of DBT dodecane solution (1000 sulphur ppm) and 2 ml of acetonitrile.

It was bring at 60 °C for a few minutes under vigorous stirring, 0.533 ml of 3% aqueous H_2O_2 solution was added and left under stirring for 24 hours.

Sample of the apolar phase were withdrawing every hour and analyzed by HPLC to evaluate DBT conversion and residual sulphur level.

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