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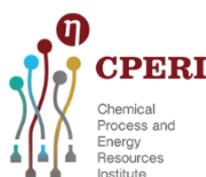
Young Researchers

October 5th 2022

CPERI/CERTH, Thessaloniki,
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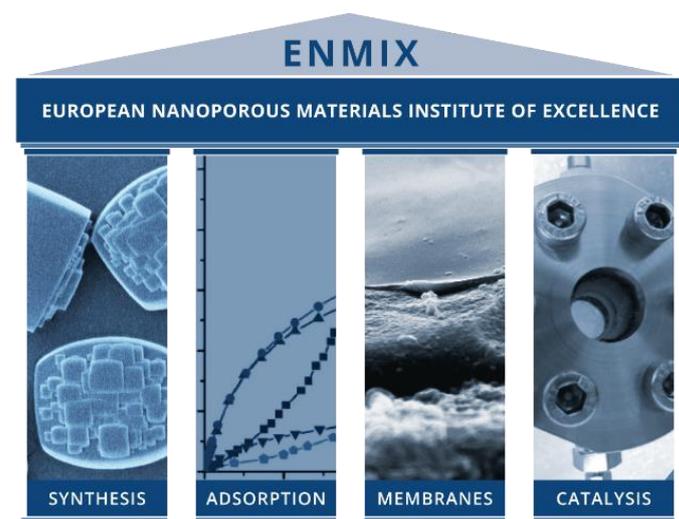
8ENMIX
Nanoporous Materials Research in Europe



Book of abstracts

9th meeting of ENMIX YR October 5th, 2022

scientific network on nanoporous materials



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Improvement Of Industrial Cu/Zn and Cu/Zr Catalysts Used For The High-Pressure Methanolization Of CO₂

M. Benz^{1*}

1) University of Stuttgart, Institute of Technical Chemistry, Stuttgart, Germany

*Michael Benz, Pfaffenwaldring 55, 70569 Stuttgart, michael.benz@itc.uni-stuttgart.de,
+49 711 685 60013.

The economic importance of methanol continues to increase, especially in the field of renewable energy storage. In this work, we want to investigate catalyst systems, which are already in use in the industry, in terms of their surface sites and reaction mechanism. Furthermore, these catalysts are to be further developed to improve the following two main points: 1) Improvement of spacetime-yield by acceleration of the rate-determining step; 2) Prevent/Slowing down of deactivation through sintering of copper surface. The proposed active site for the reduction of carbon dioxide is a reduced zinc(I) or zirconium(III) site on the catalyst[1]. Previously, hydrogen must be adsorbed to a surface copper atom which is then reducing the zinc or zirconium via hydrogen spillover. To get to point one, the mechanism of the rate determining step, which is the reduction of the zinc/zirconium by hydrogen spillover, is investigated via use of defined hydride donors and their deuterated analogues. This was previously published by the group of D. Estes for the reduction of molybdenum oxide using vanadium hydride complexes [2]. Further, the kinetic study of the reduction with defined hydrides will be done for zinc/zirconium and also the industrial as well as the newly synthesized catalysts. In addition, model complexes with reduced zinc and zirconium centers will be tested in small batch reactions for their reactivity towards conversion of carbon dioxide to methanol to verify the purposed active site. To point two, the industrial catalyst is composed by zinc oxide, aluminum oxide and copper by coprecipitation of all three metals at once [3]. Due to the synthesis method a large quantity of zinc is present in the material, which by the influence of temperature will lead to a sintering of the copper on the surface of the nanoporous material. Thus, an improvement of the TON can be achieved by reducing the possibility of sintering. One approach to this is the coprecipitation of copper and aluminum oxide with a subsequent immobilization of zinc on the surface via SOMC and being below the critical amount of zinc on the surface for sintering the copper. Last, the industrial catalyst and the newly synthesized catalysts will be tested in a high-pressure reactor setup at the university of Stuttgart to identify the connection between the results of the surface and kinetic analysis and the actual reactor tests.

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Nanostructuring The Surface Of Porous Titanium 3D Structures

J. Gys^{1,2*}, V. Meynen^{1,2}, S. Mullens²

1) *Department of Chemistry, LADCA, University of Antwerp, Wilrijk, Belgium*

2) *Unit SMAT, Flemish Institute for Technological Research (VITO), Mol, Belgium*

**corresponding author, Boeretang 200, 2400 Mol (VITO), janne.gys@vito.be, tel. +32 14 33 54 28.*

Porous titanium structures are widely used (especially as implant¹) and their potential is further extended since the development of several additive manufacturing technologies. Tailoring the surface characteristics, including the surface topography and chemistry within a 3 dimensional porous architecture is considered as an essential step to improve the performance and expand the application field of titanium based materials.^{2,3}

Several nanostructuring technologies for titanium have been reported, and the more advanced approaches enable both full control of the surface structural characteristics and its chemistry. Examples of titania nanostructures include titania nanotube arrays, nanowires and nanosheets or porous layers of different layered titanates. Application for such materials include bone implants, as catalyst material or within energy devices.

However, the nanostructuring approach is typically applied on flat surfaces (i.e. 2D). Therefore, the main aim of this research is to transfer these nanostructuring approaches onto porous 3D micro-extruded titanium. The resulting advanced functionalities of a nanostructured 3D monolith will open up new application domains, with its innovation potential in the specific combination of the architecture of the monolith and its nanostructured surface (i.e. hierarchical porosity). Herein, the open architecture of a 3D printed monolith prevents large pressure drops, provides an enlarged contact area and prolonged contact time compared to a dense or flat substrate, whilst the nanoporous coating and controlled surface chemistry is responsible for the selective adsorption or separation of molecules/ions (see Figure 1).

Our research focuses on the synthetic control of a nanoporous titanate layer on the surface of a 3D printed titanium (Ti) monolith by the use of an alkali treatment strategy. The alkali treatment of Ti relies on a chemical (corrosion) reaction at the surface, forming a thin porous titanate layer (meso-macropore range), as shown in Figure 1. This strategy earlier proofed to be able to generate a homogeneous (nano)porous titanate layer onto conventional Ti 2D surfaces (plates, powders, fibers,...).^{4,5} The major challenge and innovative aspect of this research is to transfer this strategy to a 3D monolith structure, to understand the synthesis-properties correlation and to find appropriate characterization techniques to examine the effectiveness and resulting porous layer characteristics of the alkali treatment approach onto the 3D structures.

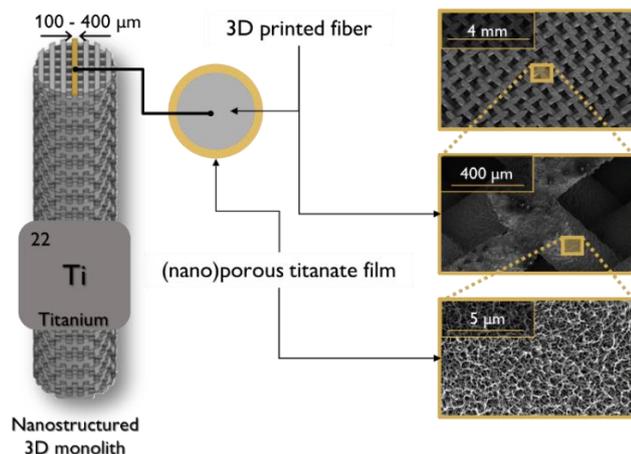


Figure 1: Left: schematic representation of a 3D printed Ti monolith composed of a mutual stacking of Ti fibers, which contain a thin nanoporous film after alkali treatment. Right: SEM images of the cross-section of a nanostructured 3D printed Ti monolith after alkali treatment, indicating the hierarchical porous structure.

As a bridge towards investigating the impact of the unique 3D monolith features (fiber stacking design, fiber crossing areas, ...) on the resulting material properties, Ti powders are deployed as substrate, from which the influence of geometric surface area (GSA) and particle size (i.e. substrate curvature) can be extracted. Primary experiments indicate an influence of the Ti GSA per mol base on the kinetics of the alkali mechanism and obtained layer morphology. The observations are based on in-situ H₂ gas development experiments (correlated to the dissolution of Ti from the substrate) and Ti concentration measurements in the alkaline solution in function of time, as well as SEM images of the obtained coated powder particles.

In general, progression has been made in gaining insight in the synthesis-properties correlation, based on alkali treatment of powders, by investigating the impact of Ti GSA on the alkali mechanism and the resulting layer morphology. However, a challenge of this research remains to find parallel characterization techniques allowing to make unambiguous conclusions about the layer homogeneity (considering chemistry, purity, porosity, layer thickness,...) and its correlation to application in sorption processes (or other potential applications).

This abstract is written with the intention to give a presentation during the young researchers event on the 5th of October, as well as to present a poster during the Enmix workshop from the 6th till 7th of October.

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P-doped carbon derived from phytic acid and its application for benzyl alcohol oxidation: Effect of the synthesis route on catalytic activity

E. S. Duran-Urbe, J. J. Villora-Picó, E. V. Ramos-Fernández, A. Sepúlveda-Escribano

Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica – Instituto Universitario de Materiales de Alicante, Universidad de Alicante, Alicante, Spain
**Edgar.duran11@ua.es, Apartado 99, E- 03080, +34 965903400-2048*

Phosphorus-doped carbon are promising materials for being used as metal-free catalysts in the production of chemicals and for biomass transformation, mainly due to the acidic character of the phosphorus species [1]. Several studies have shown that there is a dependence between surface phosphorus species and catalytic activity, with the phosphorus bound within the graphitic structure being the most interesting species [1]. This is associated with the fact that the introduction of an atom with a large atomic radius, such as phosphorus, induces a modification in the electronic properties of the material, as well as in its adsorption/desorption capacity [2]. However, the introduction of phosphorus into the carbon structure is difficult to achieve, due to the aforementioned large atomic radius of P [1]. Therefore, the synthesis route has important consequences on the catalytic activity of the carbon, because depending on the precursors and the treatment, different phosphorus species can be obtained.

The most common methods for the preparation of P-doped carbons include the carbonization of phosphorus-containing precursors and the modification of already prepared carbons with dopant species, such as phosphoric acid and phosphorus pentoxide, among others [1], [2]. The use of phytic acid (PA) as a phosphorus precursor is of great interest because it is an inexpensive, biomass-derived compound with a large amount of phosphate groups [3],[4].

On the other hand, the selective oxidation of alcohols with molecular oxygen is one of the most important and challenging reactions in organic chemistry, being the selective oxidation of benzyl alcohol (BA) one of the most studied reactions [4], [5]. It has been observed that, depending on the catalyst used and the conditions of the catalytic system, different reaction products such as toluene, benzoic acid and benzaldehyde, among others, can be obtained, being benzaldehyde (BAD) an industrial intermediate of great interest.

In this work, we present the preparation of phosphorus-doped carbon catalysts using phytic acid as dopant agent. The synthesis of the materials were carried out using commercial mesoporous carbon (RGC-30) and PA as precursors, which were pyrolyzed in an inert atmosphere at different temperatures. In addition, the effect of pretreatment before pyrolysis and the carbon/doping agent ratio were studied.

After the pyrolysis treatment, the presence of phosphorus in the carbon was observed by XPS, which is characterized by peaks from 132 to 134 eV in the P 2p region in all catalysts. Furthermore, it could be observed that, depending on the pyrolysis temperature, the amount of PA and the pretreatment of the precursors, different phosphorus functional groups are obtained. The synthesis route in which phytic acid is polymerized on RGC-30 was found to be the most suitable, resulting in surface

phosphorus with a binding energy close to that of C₃PO (132 eV) (Fig. 1). It was also observed that the textural properties of the activated carbons are affected by the amount of precursor, such that large amounts of PA (RGC30/PA weight ratio 1:2) decrease the surface area and mesopore size. When testing the catalytic activity for the oxidation of BA (at 120 °C), it was observed that, independently of the pyrolysis treatment of the catalyst, a selectivity for BAD of more than 99% is obtained. The pyrolysis temperature and the pretreatment of the precursors affect the catalytic activity considerably, with the catalyst polymerized at 180 °C and pyrolyzed at 900 °C (RPA PP180 P900) showing the highest conversion after 24 h of reaction (41.9 %).

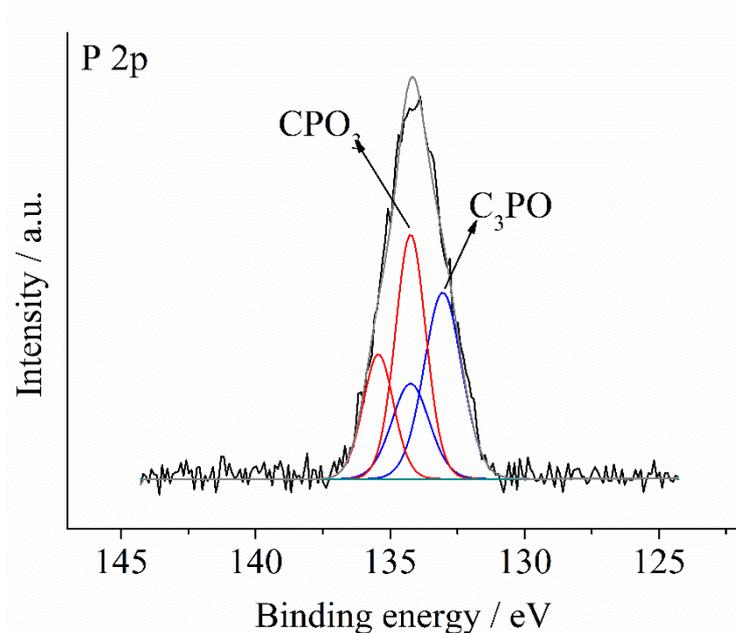


Figure 1. High-resolution XPS spectra of the P 2p for the RPA PP180 P900

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Synthesis Of Porous CuO-CexZr1-xO2 Catalysts For Combustion Of Volatile Organic Compounds

W. Van Hoey^{1*}, I. Majewska², A. Rokicińska², P. Kuśtrowski², P. Cool¹

1) *Laboratory of Adsorption and Catalysis, Department of Chemistry, University of Antwerp, Wilrijk, Belgium*

2) *Department of Chemical Technology, Jagiellonian University, Krakow, Poland*
**Universiteitsplein 1, Wouter.VanHoey@uantwerpen.be, +3232652353.*

Volatile organic compounds (VOCs), which by definition are organic compounds with a boiling point ≤ 250 °C at atmospheric pressure, are amongst the major contributors to global air pollution. VOCs are emitted from a wide variety of sources and play an important role in aerosol, photochemical smog and ground-level ozone formation, hence contributing to global climate change. Besides their impact on the environment, VOCs also pose a threat towards human health, since many VOCs are carcinogenic, mutagenic and teratogenic. Due to their toxic nature, strict regulations regarding VOCs emissions have been implemented. To comply with these regulations, efficient techniques of VOCs elimination from polluted air, including adsorption, membrane separation, thermal oxidation, (photo)catalytic combustion, have attracted extensive research. From these methods, catalytic combustion is believed to be the most promising due to its low cost, low operational temperature (200 – 500 °C) and limited formation of by-products.[1]

At present, noble metal based catalysts are considered to be the most efficient for the VOCs abatement. However, the high cost of these materials has led scientific research towards exploring cheaper transition metal oxide containing catalysts. Ceria and cerium based materials have been widely used in catalytic processes (CO-PROX, automotive three-way-catalysis, water-gas shift reaction, etc.) owing to their high redox activity and oxygen storage capacity (OSC). The latter is caused by the presence of lattice defects in the crystal structure, which induce oxygen mobility. As a result, besides Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) also Mars-van Krevelen (MVK) mechanisms can be activated in the oxidation reactions. Hence, this is why ceria and cerium based materials are of specific interest for the VOCs combustion.

According to literature, the OSC of the widely used ceria can be enhanced significantly by incorporating zirconium ions in the crystal lattice. The smaller size of a Zr⁴⁺ cation (ionic radii of 0.84 Å compared to 0.97 Å for Ce⁴⁺) modifies the cubic fluorite structure of CeO₂, which results in an enhanced OSC and oxygen mobility, improving the redox properties of the material.[2] Moreover, the addition of zirconia also improves the thermal stability of ceria. Therefore, in this research focus is put on the synthesis of Ce/Zr-oxide based catalysts for the VOCs combustion.

In an attempt to enhance the VOCs combustion properties of Ce/Zr-oxide based materials, specific amounts of Cu were added. Cu is cheap, has good redox properties and is known to have a strong synergistic effect with CeO₂. In addition, the activity of CuO/CeO₂ catalysts depends on the CuO dispersion and/or on the extent of interaction with the support.[3] Therefore, in this research Cu was deposited by using

a water based ammonia driven deposition precipitation method, which ensures a strong metal-support interaction and high stability of the deposited CuO sites.[4] The influence of the catalyst composition CuO-CexZr1-xO2 (x = 0; 0.25; 0.5; 0.75; 1) on the properties of active phase and its catalytic performance in the toluene combustion was studied.

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IMPROVING THE PHOTOCATALYTIC ACTIVITY OF TiO₂/P25 BY USING DIFFERENTLY STRUCTURED CARBON MATERIALS AS A CO-CATALYST.

C. Abreu-Jaureguí^{1*}, J. Silvestre-Albero¹, A. Sepúlveda-Escribano¹

1) Laboratorio de Materiales Avanzados/Dpto. Química Inorgánica/Instituto Universitario de Materiales Avanzados/Universidad de Alicante, Alicante, España.

**corresponding author, coset.abreu@ua.es.*

Photocatalysis is a greener and sustainable option to degrade organic contaminants into relatively harmless by-products. Rhodamine B is a particularly harmful organic dye that is carcinogenic and highly toxic to aquatic and human life. Therefore, this colorant was chosen as a representative industrial contaminant for this investigation. Among the best catalysts for pollutants degradation are semiconductors like TiO₂. Commercially known as Degussa P25, this material has been extensively studied due to its relatively low cost, photochemical stability, and high photocatalytic activity without generating secondary contaminants. However, the downside of this catalyst is the rapid recombination of electron-hole pairs that comes from having a wide band gap and limits its photocatalytic application to only the UV light range. Since the main purpose of photocatalysis is to use direct sunlight (43% visible, 4% UV) there is an obvious need to modify TiO₂ in order to maximize its use. The latest research in this field had been focused mainly on overcoming these issues by designing different semiconductors with noble metals. These materials are expensive, non-abundant, and harmful to the environment. Therefore, it's crucial to explore other non-metal and eco-friendly resources that also present excellent photocatalytic performance under visible light. Current studies have anticipated that carbon-based nanostructures exhibit a promising performance (e.g., graphitic carbon nitride (CN), partially reduced graphene oxide (rGO), graphite (GI), and single-walled carbon nanotubes (SWCNT)). Combining these materials with P25 can address the problems of fast recombination and solar energy utilization by forming a type-II heterojunction. However, there is a gap when it comes to explaining the photocatalytic behavior difference displayed between these carbon catalysts at the structural level.

Based on these premises, the present study proposes a comparative analysis of four carbonaceous materials of varied structures (CN, rGO, GI and SWCNT) as modifying agents of commercial titanium dioxide TiO₂ (P25) -P25- for the photocatalytic degradation of Rhodamine-B. The prepared catalysts were synthesized following the same wet impregnation method using an excess of methanol, 90% of P25, and 10% of carbonaceous material. Once obtained, they were analyzed by different physicochemical techniques to evaluate their structure and morphology. Specifically, N₂ adsorption, XRD, XPS, TEM, RAMAN, and UV-Vis were applied. The photocatalytic experiments considered four different lighting environments: visible, ultraviolet, artificial solar (4% UV), and dark as a reference. At the end of the analysis time, the samples were centrifuged and analyzed in a UV-Vis spectrophotometer taking as reference the characteristic peak of RhB, which is detected at 554 nm.

The characterization of the synthesized catalyst showed that they are mostly low

porosity materials, except in the case of SWCNT. The specific surface BET ranges from 55 (GI-P25), 56 (CN-P25), 85 (rGO-P25), and 120 (SWCNT-P25) m²/g. Regarding the composition of the catalysts, it was known that crystallographically the predominant peaks correspond to the P25 anatase and rutile phases. On the contrary, by TEM the presence of carbonaceous materials and P25 can be clearly observed, as well as a good dispersion between them. As for XPS analysis, it was noticed a significant shift in the P25 characteristic peaks for rGO-P25 and SWCNT-P25 samples, meaning a strong interaction between both species, which was later confirmed by RAMAN. Although all synthesized catalysts degrade Rhodamine-B in less than 2 h depending on the type of light to which they were exposed (Fig. 1), the combinations (i) partially reduced graphene oxide/P25 and (ii) single-walled carbon nanotubes/P25 showed the best results. This outcome can be justified considering the dual properties of the synthesized catalysts due to the combination of an excellent adsorption performance and improved photocatalytic activity. In a few words, it was possible to synthesize a catalyst that, in atmospheric conditions (TPEA, artificial sunlight) improves the photocatalytic activity of the currently most used material for these purposes by itself, P25.

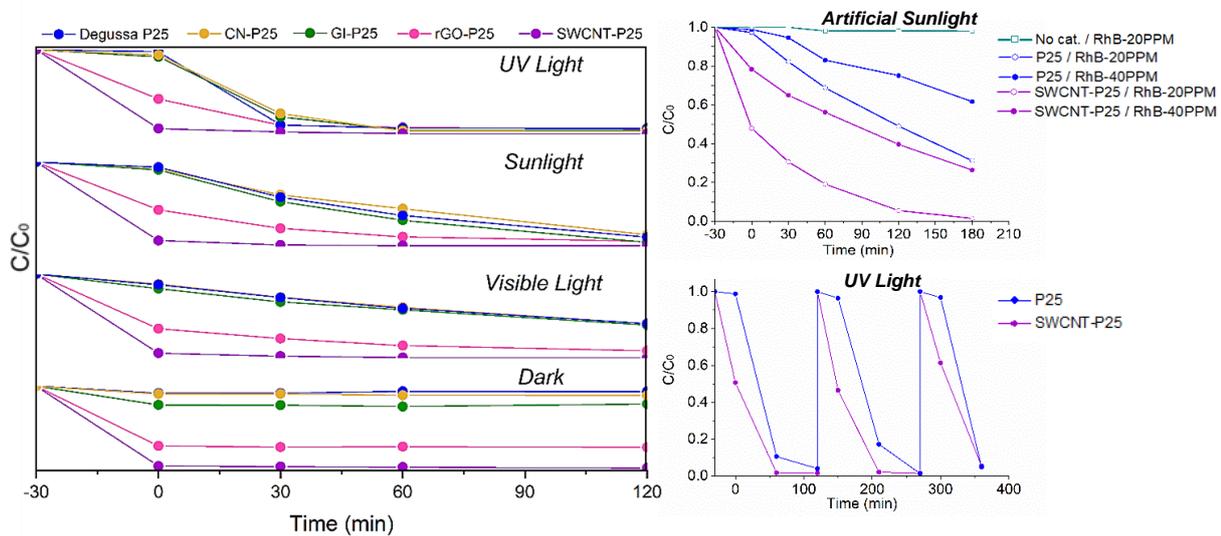


Figure 1. Photocatalytic performance of all synthesized catalysts under different RhB concentration.

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The Reduced Stability of Aminomethylphosphonic Acid Grafted on Titania Related to the Phosphorous-Carbon Bond Strength

Rui An¹, Léon Luntadila Lufungula², Frank Blockhuys², Vera Meynen^{1,3,*}

- 1) *Laboratory of Adsorption and Catalysis (LADCA), Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium.*
 - 2) *Structural Chemistry Group, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium.*
 - 3) *Sustainable Materials, Flemish Institute for Technological Research (VITO NV), Boeretang 200, 2400 Mol, Belgium.*
- *corresponding author: vera.meynen@uantwerpen.be*

Organophosphonic acids (PAs) functionalized metal oxides have found their way in many application areas including separation technologies, catalysis, optoelectronics, and medical applications[1]. As one of the most used inorganic supports, titania offers structural properties, high chemical and mechanical stability. The organic functionalities in the PAs which is responsible for the specific interactions can also be changed according to the application scenarios. So far, PAs with an alkyl, aryl, or aminoalkyl functional group grafted on titania has been investigated in depth[2-4]. However, the role and the impact of the amine group in the PAs have not yet been fully revealed. It is necessary to understand the impact and differences introduced by the amine group since it is essential to customize the surface properties towards application. In this work, TiO₂ P25 functionalized with alkyl-PAs and aminoalkyl-PAs are investigated with in-situ DRIFT, TGA, and DFT calculations. The in-situ DRIFT measurements measured with increasing temperatures show that there is formation of P-H bond above 250 °C in the aminomethylphosphonic acid (AMPA) grafted on TiO₂ P25 after the breakage of the P-C bond (Fig.1), which is not the case for the other PAs. The TGA results agree with the reduced thermal stability of AMPA modified samples compared to the samples of the other PAs. DFT calculations indicate that the P-C bond length of the most energetically favourable AMPA configuration on anatase (101) surface is 1.833 Å which is significantly longer than the other PAs such as 2-aminoethylphosphonic acid (2AEPA) (Fig.2). The results indicates that the P-C bond stability of AMPA samples is lower compared to the other PAs which could offer unique properties and impact its applicability in certain scenarios.

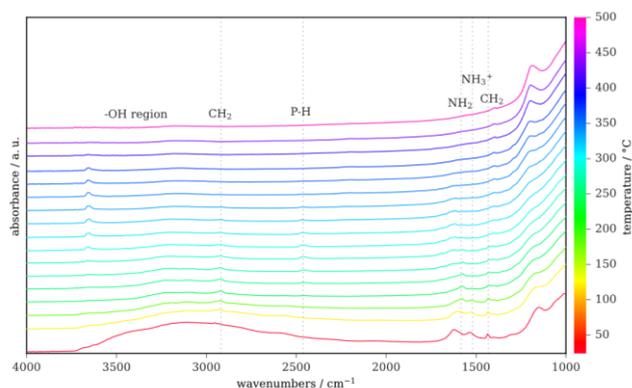


Fig.1 DRIFT spectra of an AMPA sample

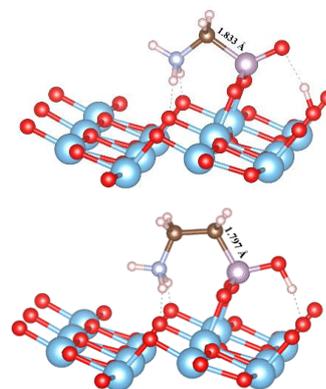


Fig.2 AMPA and 2AEPA on anatase(101) surface

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H₂S removal from biogas at low temperature on Cu- and Mg-modified activated carbon honeycomb monoliths

E.M. Cepollaro^{1*}, D. Caputo², N. Gargiulo³, F.A. Deorsola⁴, S. Cimino¹, L. Lisi¹,

1) Istituto di Scienza e Tecnologia per l'Energia e la Mobilità Sostenibili, Consiglio Nazionale delle Ricerche, Napoli, Italy

2) Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Napoli, Italy

3) Università degli Studi di Napoli Federico II, Napoli, Italy

4) Dipartimento Scienza Applicata e Tecnologia, Politecnico di Torino, Torino, Italy

** Via G. Marconi 4, 80125 Napoli, Italy, elisabettamaria.cepollaro@stems.cnr.it, tel. +39 0817682220, fax +39 0817682262.*

The purification of reformed gas, natural gas and raw biogas from hydrogen sulfide is a mandatory step before their use as fuels as it is a toxic compound, corrosive for engines and fuel treatment devices and poisonous to catalysts also in small concentrations. Due to its easy management, high efficiency and low cost, adsorption is one of the most effective techniques for H₂S removal. In particular, Activated Carbons (ACs) are excellent candidates as good H₂S absorbents due to their surface chemistry, high internal surface and porosity. ACs are generally used in powder form, however, as high pressures are required, their application in structured form is preferred. Production of ACs in structured form generally requires the use of binders which, while improving the mechanical properties of the sorbents, reduce the adsorption capacity due to the partial blocking of porosity. Otherwise, the introduction of suitable metals can lead to the improvement of the original properties of the AC [1, 2].

In this work, commercial honeycomb ACs were functionalized with copper and magnesium oxides both separately and mixed in order to improve H₂S capture capacity under different operating conditions.

The sulfur capture capacity and the different oxidation reactions by varying the two metals were evaluated through dynamic catalytic tests (100ppmv H₂S) at room temperature in the presence of humidity and O₂. Depending on the nature of the metal used, the performance of the catalyst was significantly different. The presence of basic MgO promotes the formation of elemental sulfur through a faster path than the deeper oxidation mechanism promoted by CuO, which leads to the formation of sulfates / sulfuric acid in addition to elemental sulfur. Mg allows easier dissociation of H₂S into HS⁻ and H⁺ which improves the capture capacity of ACs in the presence of wet streams compared to Cu-modified ACs for the same load level.

The mixed Cu-Mg sorbents therefore inherited the fast kinetic characteristics of MgO, promoted by the presence of water vapor, and the oxidation activity of CuO, also exercised in dry conditions.

Adsorption of N₂ at -196 ° C, PSD, XPS, TG-MS have been performed on honeycomb catalysts, both fresh and spent, in order to study the specific nature of the S species formed during the catalytic adsorption. In particular, TG-MS experiments from exhausted sorbents allowed the speciation of adsorbed sulfur species, as shown in Figure

1.

The original porous structure and the performance of the modified AC monoliths was restored through a thermal treatment up to 620°C under a flow of inert gas which led to the decomposition of sulfate species at a lower temperature and the evaporation of elemental sulfur at higher temperature allowing a complete regeneration of the spent sorbents.

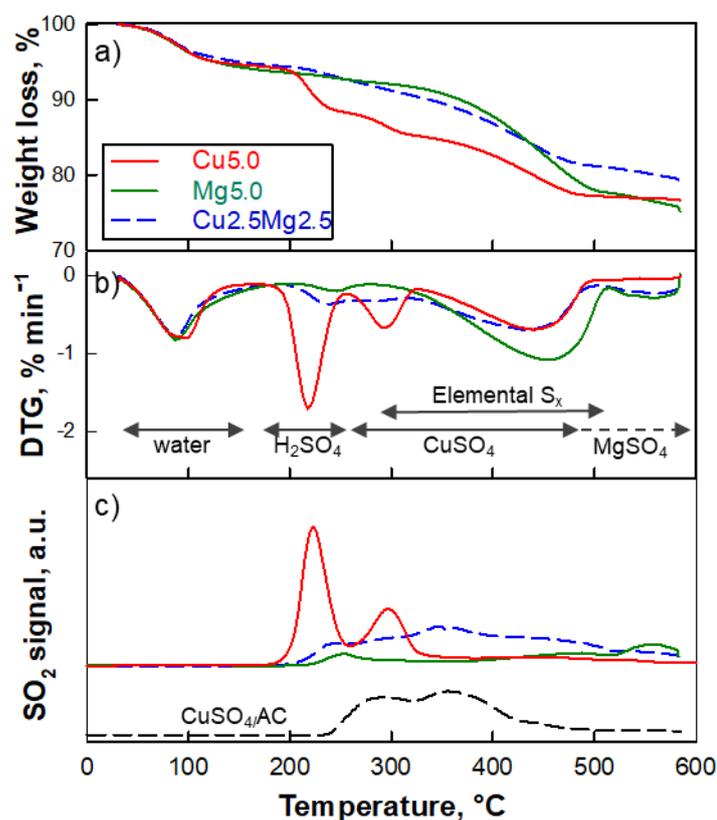


Figure 1. TG (a), DTG (b) profiles and corresponding MS traces for SO₂ ($m/z = 64$) in the evolved gas during the temperature programmed desorption under inert flow from exhausted Cu5.0, Mg5.0 and Cu2.5Mg2.5 honeycomb catalytic AC sorbents. The MS profile for CuSO₄ dispersed onto activated carbon is reported for reference.

Therefore these structured AC monoliths functionalized with copper and/or magnesium can operate several capture cycles without detectable loss of capture capacity releasing only SO₂ and S and are excellent candidates for the H₂S capture process at room temperature for biogas purification.

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Supported Pd and Pt Catalysts for Enyne Cycloisomerization

E. Wimmer^{1*}, D. P. Estes

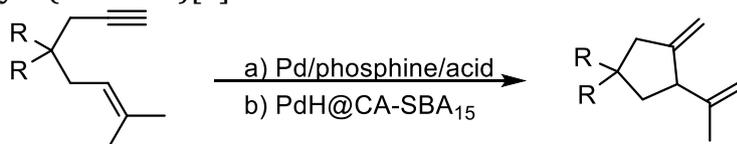
1) University of Stuttgart, Institute of technical chemistry, Stuttgart, Germany

*corresponding author, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart,
+49 711 685 64309

Cyclization reactions have always been an art in organic chemistry. Cycloisomerization is a special form in which a ring with perfect atomic economy is introduced.

The cycloisomerization of enynes has been studied intensively over the last 100 years, from thermal reactions to palladium-, Ir-, and Pt-catalyzed reactions [1]. Toste and Trost and co-workers have studied palladium catalysis intensively and synthesized active and (enantio-)selective palladium hydride catalysts with up to 88 ee% using a Pd/phosphine/acid system (Scheme 1). The major drawbacks of these reactions are the rapid deactivation, the low recyclability of the catalyst and the required high catalyst loading (2.5-5 mol%) [2].

We have previously shown in our group that Pt(0) complexes can be immobilized on a metal oxide surface by an oxidative addition reaction with concomitant formation of the active catalyst (SiO-Pt-H)[3].



Scheme 1: Enyne cycloisomerization by a) a typical catalyst system and b) a proposed supported catalyst.

With this strategy, highly active and selective immobilized Pd-H catalysts can be synthesized and characterized by standard techniques in SOMC (IR, MAS NMR, XAS) (Scheme 1b). Pd(0) complexes also show a tendency to react with chiral acids and alcohols in an oxidative addition reaction to form a Palladium hydride[2]. The use of enantiopure acids/ alcohol and immobilization of these ligands on mesoporous material such as SBA 15 should enhance the equilibrium association of Pd(0) complexes and increase activity and enantioselectivity due to confinement effects (Scheme 1b).

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Evaluation of ZIFs as Potential Heat Storage Materials Using Water and Ethanol as Working Fluids

C. Byrne^{1*}, N. Zabukovec Logar^{1,2}

1) *Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Ljubljana, Slovenia.*

2) *School of Science, University of Nova Gorica, Nova Gorica, Slovenia.*

**corresponding author, ciara.byrne@ki.si, Tel: +386 1 4760 286*

The increasing demand of heating/cooling is of grave concern due to the ever-increasing population. As a result of this, there has been a growing interest in using environmental friendly methods for meeting the energy supply/demand. One method that addresses this issue and uses renewable energy is Thermochemical Energy Storage (TCES), which is based on the reversible chemical reactions and/or sorption processes of gases in solids or liquids. The major benefits of using TCES is that it only shows a negligible amount of heat loss and it can reach a higher energy storage density compared to sensible heat storage and phase change materials storage. Additionally, TCES has the ability to exploit solar thermal energy and low-temperature industrial waste heat. At present, studies examine traditional (e.g. zeolites) and innovative (e.g. aluminophosphates, metal-organic frameworks (MOFs) and composites) sorbents for sorption thermal energy transformations. However, the inability to make novel adsorbents that can be efficiently utilised under specific parameters for 'real-life' applications is the reason why there is continuous interest in this field by researchers and why a significant amount of work is still required [1]. Recently, we have focused on the evaluation of Zeolitic imidazolate frameworks (ZIFs) as porous adsorbents in low T sorption-based TES (sun/waste heat) applications. ZIFs are subgroup of MOFs and are comprised of transition metal ions (Zn, Co, etc.) and imidazolate linkers. The materials are considered highly stable, have highly ordered porous structures and can be shaped into glasses (e.g. monoliths). The optimisation of ZIFs for heat storage and allocation applications has yet to be extensively studied. The vast majority of these studies examine water as the working fluid, as it is readily available and the greenest solvent/adsorbate. Using ethanol instead of water as the working fluid is of interest as a study completed by De Lange et al. (2015) has shown it has many potential advantages [1]. Despite these potential benefits (e.g. use at lower temperature), ethanol based sorption studies have rarely been explored. In general, the main criteria for selecting ZIF structures as adsorbents are the pore entrance size and the pore/cage capacity. Additionally, the hydrophobicity of the ZIF also has impact on adsorption capacity. These can be fine-tuned by introducing local structural features, which effects adsorbate-adsorbent interactions largely. Finally, a recent study completed on the uptake of ethanol, methanol and water for two ZIFs by Byrne et al. (2021) concluded that the functional groups of linkers also play an important role on the end application [2]. In the presentation we will focus on the optimized synthesis, characterisation and sorption-based studies of ZIFs with varying pore entrances, pore capacities and hydrophobicity, including ZIF-8, -62, -71, -74, -76, -90 and -93. The structural properties of the ZIFs were studied using PXRD, TGA, SEM and N₂ physisorption while the mmol/g of adsorbate uptake and desorption enthalpy were analysed using IGA-100 gravimetric water and ethanol sorption analyser and DSC respectively. The structural studied show the presence of phase pure ZIFs while the

sorption-based studies show that there is great potential for using ZIFs for TCES. Finally, the sorption-based studies show the importance of the selection of the adsorbent-adsorbate pairs.

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Sulfur-Doped Carbons as Metal-Free Catalysts for Nitroarenes Hydrogenation

G. Gil-Muñoz, J.J. Villora-Picó*, M.M. Pastor-Blas, A. Sepúlveda-Escribano

*Laboratorio de Materiales Avanzados, Instituto Universitario de Materiales de Alicante –
Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080
Alicante, Spain
jj.villora@ua.es.

The hydrogenation of nitroarenes to obtain the corresponding anilines is a high interest reaction because they are precursors of products with high added value such as dyes, agrochemicals, and drugs [1]. The development of new heterogenous catalysts for organic synthesis reactions is a high interest topic because of the enormous advantages they provide in comparison with the homogenous catalysts, thanks to its easy recovering and recycling. Metal-based catalysts supported on carbons are among the most used ones in these types of reactions, due to their good results in activity and selectivity, and also their low cost and easy obtention.

In this sense, carbons doped with heteroatoms are a good alternative. In bibliography, a large variety of studies related with nitrogen doped carbons can be found. Nitrogen is an atom with similar size to carbon, so it is easily inserted in the carbon structure, and its free electron pair can form π conjugated bonds with π bonds from the carbon lattice, this improving the catalytic properties [1]. Moreover, there are works in which also sulfur is inserted, because it is an atom with a higher size and different electronegativity and electronic structure than nitrogen. This fact favors the creation of defects that modify the electronic configuration of the material as well as the surface area and active sites [2].

However, reports about sulfur-doped carbons as metal-free catalysts is scarce, so the motivation of this work is the preparation of sulfur-doped carbons from polythiophene and to evaluate their catalytic activity in the hydrogenation of 1-chloro-4-nitrobenzene. The carbon prepared has been activated with steam at different times and temperatures.

Polythiophene preparation has been performed through an oxidative chemical polymerization of the monomer (thiophene). Once the polymer is obtained, the sample is pyrolyzed at 900 °C for 4 h and activated subsequently with steam at different temperatures and times to evaluate the effect of the synthesis conditions on its properties and catalytic activity. The nomenclature of the samples is: PT-P9-S(Activation T (°C)/100)-(Activation time in h). For instance, sample PT-P9-S8-4 has been activated at 800 °C for 4 h. Catalytic activity of the samples has been evaluated in the hydrogenation of 1-chloro-4-nitrobenzene reaction. The prepared materials were characterized using different techniques such as FTIR, TGA, nitrogen adsorption at -196 °C, XPS and RAMAN spectroscopy.

The polythiophene pyrolyzed at 900 °C presents a type I isotherm (Figure 1) typical of microporous carbons. The activation at 700 °C does not affect to the porous

properties. Once the activation temperature is increased to 800 °C, the porosity starts to develop, increasing with the activation time. This activation generates microporosity. However, when the temperature increases to 900 °C, the microporosity begins to widen forming mesopores as it can be appreciated in Figure 1.

Also it is important to study the surface chemistry due to the fact that the processes related with heterogeneous catalysis take place in the surface. For that purpose, the prepared samples were characterized by XPS. In Table 1 it can be observed that the polythiophene pyrolysis generates sulfur- doped carbons. Furthermore, it can be determined how the sulfur amount decreases after the activation processes, and a higher temperature generates a negative effect on the sulfur amount. However, the activation time does not produce a significant effect on the sulfur content, which remains nearly constant. In the individual deconvolution for S 2p_{3/2} appears one peak around 163.9 eV which is assigned to the presence of S in sulfur bridges (C-S-C) [3] which indicates that the introduction of sulfur has been done successfully.

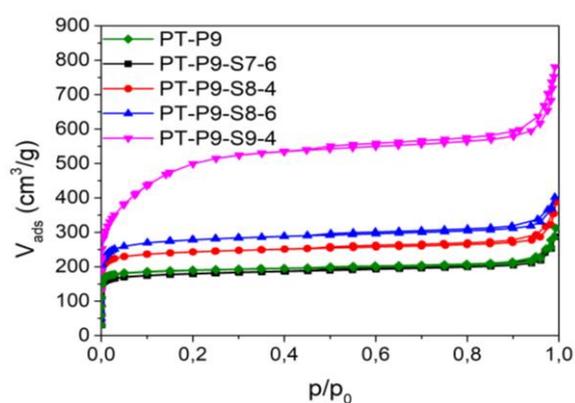


Figure 1. N₂ adsorption isotherms at 77 K

Table 1. Atomic amount determined by XPS

Sample	C 1s (% at.)	O 1s (% at.)	S 2p _{3/2} (% at.)
PT-P9	95.0	2.5	2.5
PT-P9-S7-6	95.2	2,5	2.3
PT-P9-S8-4	95.5	2.8	1.7
PT-P9-S8-6	96.2	2.2	1.6
PT-P9-S9-4	97.0	2.0	1.0

Once the material was characterized, its catalytic activity was evaluated in the hydrogenation of 1-chloro-4-nitrobenzene. The results are shown in Figure 2, and demonstrate that the catalysts are active in the reaction without the necessity of a metallic phase. Moreover, an increase in activity is observed with the increase of the activation temperature, demonstrating that the activation treatments are beneficial and, instead of the loss of surface sulfur, the improvement in the porous properties provokes an improvement in activity. In all cases, the selectivity to the hydrogenation of the nitro group was a 100 %.

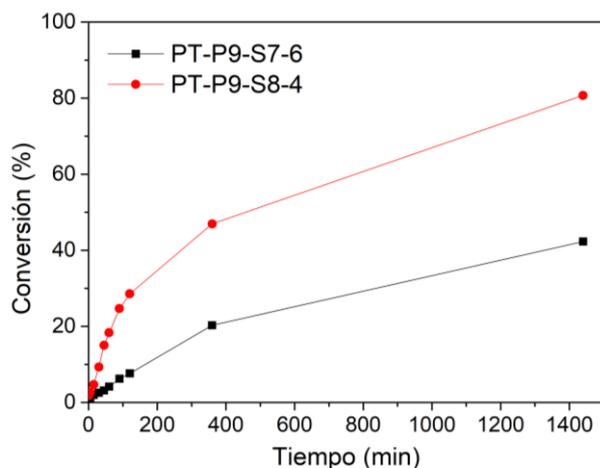


Figure 2. Results of the catalytic test for the hydrogenation of 1-chloro-4-nitrobenzene

From this work it can be concluded that sulfur-doped activated carbons have been obtained from polythiophene. Furthermore, the effect of the activation conditions has been reviewed in the porous properties and its surface chemistry. Finally, its catalytic activity has been tested in the hydrogenation of 1-chloro-4-nitrobenzene obtaining satisfactory results.

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