Katholieke Universiteit Leuven

Faculty of Bioscience Engineering

Catalytic upcycling of phthalate plasticizers

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Erasmus Dissertation
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Preface

After four years of education at Faculty of chemistry in Zaragoza and one semester at Faculty of Bioscience engineering in Leuven, I am proud to present this Erasmus Dissertation, the finale work of my Chemistry Bachelor.

Firstly, I would like to thank my tutor Simon Windels for giving me this opportunity and introduce me to phthalates and oxidative coupling a field unknown for me. This semester, he has continuously guided me along the way, providing brilliant ideas and helping me in the redaction. Secondly, I would like to thank professor Dirk De Vos and the rest of the researchers and staff at the DDV unit, who created a pleasant atmosphere to work in and helped me when I need it.

I am grateful to my family, which has always supported me to follow my goals, encouraged my curiosity and helped me grow as a person. In addition, I would like to show my love to all those friends who have had kind words and have listened to me in good and bad times, and to the University of Zaragoza, which has made my learning possible. Finally, I would like to thank the teachings I have learned, both from my classmates and my professors.

Summary

The importance of plastics - has been increasing over the last century, reaching production rates of 368 million tons in 2019. Today, the plastic economy is still dominated by a linear profile (consecutive production, consumption and disposal) as less than 30% of the produced plastics are recycled. In order to minimize the pressure on natural resources, to drastically reduce CO_2 emissions and to achieve the 2050 climate neutrality target, The European Green Deal and its "Circular Economy Action Plan" were initiated. In this report we will go deeper into the concept of legacy additives and in particular the use of phthalate plasticizers in PVC. The phthalates plasticizers were the general plasticizer used in industry, however, since that they are classified as endocrine disruptors and reprotoxic the European Registration, Evaluation and Authorization of Chemicals has implemented strict regulations for the production, handling and disposal of these components. In fact, low molecular weight phthalates are currently banned in Europe, so that the plasticizers can also not be present in recycled material, which complicates traditional recycling of flexible PVC. In this report, it was investigated whether these toxic phthalate esters can possibly be revalorized via the oxidative coupling to form 3,3',4,4'-biphenyltetracarboxylic tetraester (S-BPTT), which is used as precursor for polyimide resins.

Throughout this dissertation, the effect of the main reaction parameters on the activity (TON) and selectivity of the oxidative coupling of dimethyl phthalate has been investigated. It was in particular observed that rather drastic conditions (16 bar O_2 and ≥140 °C) are necessary to obtain a fairly active coupling system. While many solvents proved completely unsuitable for the oxidative coupling of phthalates, the addition of acetic acid to the mixture improved both the activity and selectivity of the gold catalyst. In the last steps of this work, the Au-catalyst and its preparation method was further analysed. The urea deposition method in combination with an activation step (heat treatment in air) proved to be the most suitable method to produce heterogeneous catalyst up to 8 wt.% Au. Remarkably, it was concluded that the metal loading does not affect the catalysts performance, as the chosen preparation method presumably gives rise to catalysts with the same metal particle sizes regardless of the metal loading. In the catalyst support screening, Au supported on ZrO_2 proved to be an excellent catalyst, as it combined the highest observed coupling activity with a high regio- and chemoselectivity.

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List of abbreviations

S-BPTT	3,3',4,4'-biphenyltetracarboxylic tetraester
A-BPTT	2,3,3',4'-biphenyltetracarboxylic tetraesters
BFRs	Brominated flame retardants
BeBP	Benzyl butyl phthalate
CEAP	Circular economy action plan
CMD	Concerted metalation-deprotonation
DBP	Dibutyl phthalate
DEHP	Diethylhexylphthalate
DIBP	Diisobutyl phthalate
DIHP	Diisoheptyl phthalate
DINP	Diisononyl phthalate
DMP	Dimethyl phthalate
DnOP	Di-n-octyl phthalate
REACH	European registration, evaluation and authorization of chemicals
FID	Flame ionization detector
GC	Gas chromatography
GC-MS	Gas chromatography – mass spectrometry
HBCD	Hexabromocyclododecane
HDPE	High density polyethylene
HMW	High molecular weight
LDPE	Low density polythelene
LMW	Low molecular weight
MOFs	Metal organic frameworks
rPVC	Rigid polyvinyl chloride
Pd	Palladium
pPVC	Plasticized polyvinyl chloride
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PVC	Polyvinyl chloride
PC	Post-consumer waste
PI	Post-industrial
TON	Turn over numbers
UN	United nations
VCM	Vinyl chloride monomer

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Literature study

1. Plastics

1.1 The importance of plastics

During the 20th and 21st century, plastic materials became extremely relevant, represented by their unparalleled production rates (368 million tons produced in 2019). The growing plastic importance partially results from an increasing demand for products resulting from the population growth and the rising living standards. In addition, the raw materials and production costs are often considerable lower than for other materials, such as metal or wood, making the substitution economically favourable.[1] The high plastic versatility allows the replacement of many materials with a wide range of mechanical properties, distributing plastics across virtually all industries. Nevertheless, the packaging (40 %), building and construction (20 %) and automotive (10%) sectors account for the largest shares in Europe (Figure 1).[2]

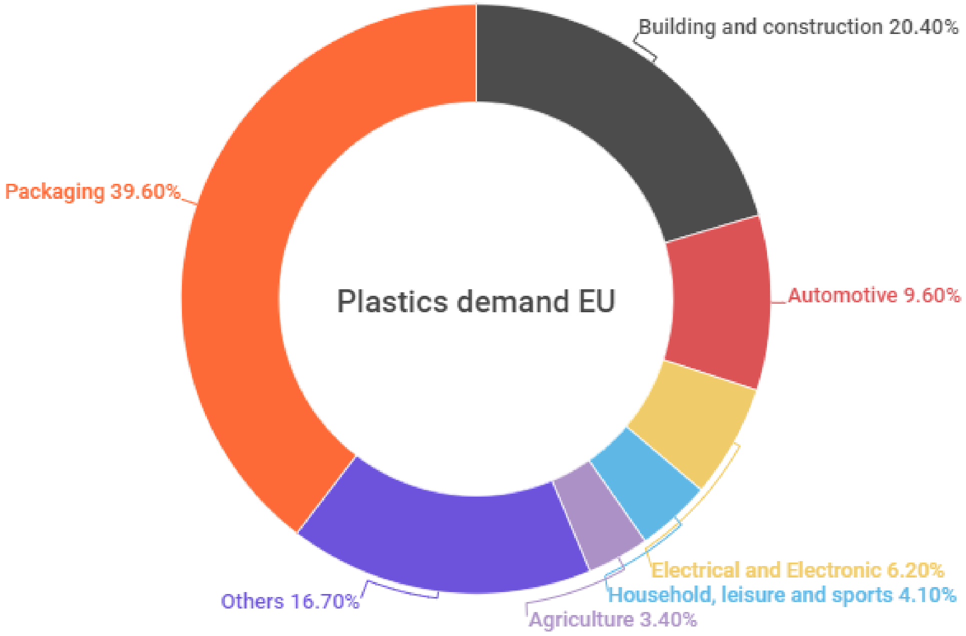


Figure 1: Distribution of European plastics converter demand by segment in 2019[1]

Plastic polymers are often classified according to their response to elevated temperatures into thermoplastics and thermosets. The internal structure of thermoplastics remains unaltered when heated, so that the plastics can be remolded several times. On the other hand, the molecular structure of thermosets is affected when the material is subjected to increased temperatures. During the heat treatment in the molding process, molecular bonds are covalently cross-linked, impeding the vibration and rotational movements of the final product. As a result, more resistant, hard and fragile materials are obtained from thermosets.[4] In order to further modify the physiochemical characteristics of plastic compounds several additives, such as plasticizers or stabilizers, are added to the plastic formulation, which can account up to 65wt% of the final product.[3,4]

1.2 The plastics economy and its environmental impact

As a consequence of the growing plastic industry, an increasing amount of the corresponding waste is produced above 29 million tonnes per year, which is generally divided in post-industrial (PI) and post-consumer waste (PC). The latter group is dominated by packaging waste, which mainly constitute out of polyvinyl chloride (PVC), high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) and polyethylene terephthalate (PET), as shown in Figure 2.[5,6]

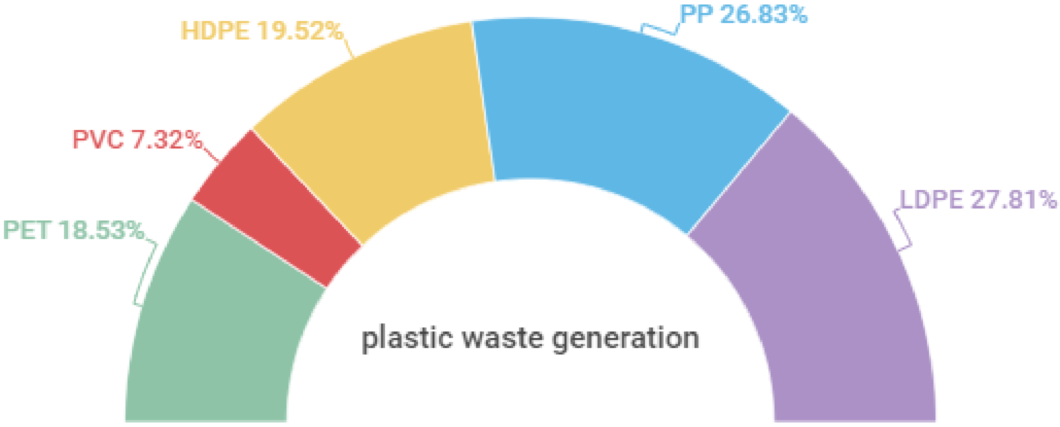


Figure 2: Relative distribution of plastic waste generated

The current plastic economy is still substantially characterized by a linear economy profile in which the plastic is subsequently produced, consumed and disposed. In 2014 for instance, less than 30% of PC waste was effectively recycled, while 40% was sent for energy recovery and more than 30% was landfilled in Europe. [1,7] Landfilling of plastic waste has wide-ranging detrimental environmental impacts including landfill settlements, vegetation damage, air and water pollution, fires and explosions.[8] Otherwise, waste incineration is also not a long-term solution as waste burning leads to environmental contamination gas emissions and volatilization of heavy metal components.[9] Recently, the European Commission started investing in a circular plastic economy, via The European Green Deal and its "Circular Economy Action Plan (CEAP)" in order to minimize the pressure on natural resources, to drastically reduce CO_2 emissions and to achieve the European Union 2050 climate neutrality target. [10,11]

1.3 Legacy additives

Plastic additives are added to the polymers during the production process, aiming to improve the processability and/or the physical and chemical properties of the final plastic product. Additives are generally categorized according to their intended function, such as heat stabilizers, antioxidants, lubricants, pigments and plasticizers. Some additives become covalently linked with the polymer matrix, while others rely on rather weak additive-polymer interactions. The latter group is rather infamous for the potential risks correlated to their leaching into the environment. Toxicological and environmental reports identified several industrially employed additives, such as brominated flame retardants (BFRs), for example Hexabromocyclododecane (HBCD), and phthalate plasticizers like Diethylhexylphthalate (DEHP), as harmful to mankind and/or the environment. Consequently, the European Registration, Evaluation and Authorization of Chemicals (REACH) in collaboration with the United Nations (UN) has gradually implemented regulations for the production, handling and disposal of these hazardous chemicals. In particular, one of the most recent objectives has been to completely phase out and prevent the recirculation of such legacy additives in commercial trade.[12] This ambition creates significant challenges as the disposal of legacy-contaminated plastics through landfilling or incineration is evidently not the most environmental friendly option. Therefore, the development of recycling techniques that permit the separation of the legacy substances from the plastic resins are of paramount importance for a truly circular plastic economy.[12] In this work, we attempt to further promote plastic circularity by transforming toxic phthalate plasticizers into re-usable and high-value compounds.

2. Plasticized polyvinyl chloride (pPVC)

2.1 PVC

Polyvinyl chloride (PVC) is the third most used plastic after polyethylene (PE) and polypropylene (PP). In 2017 the demand for PVC reached approximately 43.2 million tons and it is expected to increase to 57 million tons by 2030. [13,14] The high consumption results from the low raw material cost and the great versatility in possible end products, such as packaging materials, cleansing, textile, medical devices, pipes, windows and flooring (figure 3). [15] PVC can be classified into two main groups depending on the amount of plasticizers that has been incorporated: rigid PVC (rPVC) and flexible or plasticized PVC (pPVC). In current production, rigid PVC (65%) is mainly used in construction as in window profiles (27%) and in pipes and fittings (22%), while pPVC (26%) is mainly used in applications such as flooring (7% of total PVC produced), packaging such as flexible films (7% of total PVC produced) or medical products such as flexible tubes (2% of total PVC produced). [16]

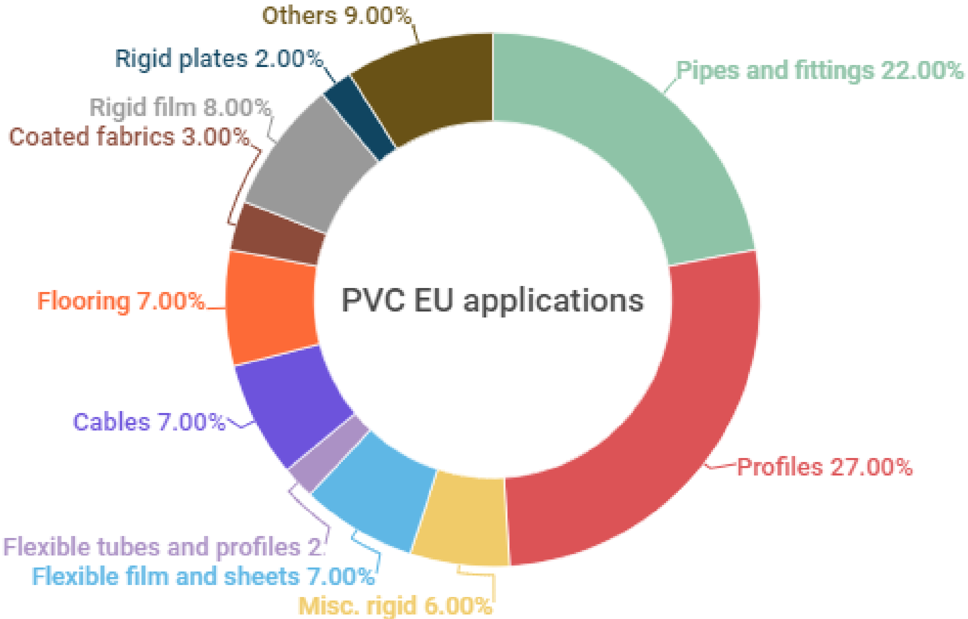


Figure 3: Relative distribution of PVC applications in EU

The structure of the PVC chain is characterized by the presence of a bulky chlorine atom that confers a polar nature to the bond (figure 4). There are three processes used for the commercial production of PVC: suspension (80% of the global production), emulsion (12%) and mass or bulk polymerization (8%), which are all based on the polymerization of vinyl chloride monomers. [17]

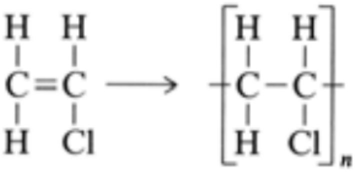


Figure 4: Reaction involved in PVC polymerization

2.2 Plasticizers

Every year, 7.5 million tons of plasticizers are produced worldwide, of which 85% is used in flexible PVC. Plasticizers are added to the PVC resin to represent up to 40wt% of the final plastic composite to modify and improve its physical properties, e.g. increased flexibility, workability or distensibility. [17, 18] During the plasticizing process, the polymer-plasticizer blend is heated until the PVC bonds weaken (70-110^{o}C), allowing the plasticizers to be intercalated into the matrix. Plasticization can be explained by the lubricity theory where the plasticizer acts as a lubricant between the PVC chains increasing their flexibility. On the other hand, the gel theory suggests that plasticizers can prevent resin-resin interactions and reduce bonding points resulting in a less interconnected polymer network. A third plasticization theory even quantifies the free volume that increases with addition of plasticizer and is consequently named the free volume theory. Plasticizers themselves can be divided into two groups: primary and secondary plasticizers. Primary plasticizers are used to reduce the glass transition temperature and thus increase the elongation and/or flexibility of the material. The latter group, on the other hand, cannot be used as the single plasticizer in the polymer matrix, often due to limited solubility, however, in the presence of a primary plasticizer the secondary plasticizers can further improve the characteristics and/or reduce the cost of the obtained flexible material. [19,20]

2.2.1 Phthalate esters

The most widely used plasticizers are low molecular weight (LMW) and high molecular weight (HMW) phthalate esters due to their high compatibility with PVC, low production cost and excellent plasticizing propieties. [18] The diesters are industrially produced by the acid-catalyzed esterification of phthalic anhydride with two units of C1-C3 alcohols. C1-C3 esters are generally not used as plasticizers due to their high volatility and resin mobility, which leads to undesired effects during both production and consumption of the plastic material. Phthalates of C4-C5 composition are also characterized by a higher volatility, but are instead used as gelling agents in combination with other esters of higher molecular mass. Diisoheptyl phthalate (DIHP) is a C7 phthalate, it balances volatility and viscosity, so that is used as a gelling agent and as plasticizer. As for C8 esters, the most widely used plasticizer is di-2-ethylhexyl phthalate (DEHP) due to its gelling characteristics, softening action and adequate viscosity properties in PVC emulsion pastes. Another C8 product is di-n-octyl phthalate (DnOP), its linear structure improves low temperature performance and confers a lower viscosity. Esters produced from C9-C10 oxo-alcohols have similar properties to C8, although higher mass results in lower plasticizing efficiency. [19]

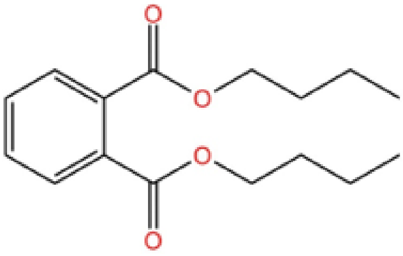
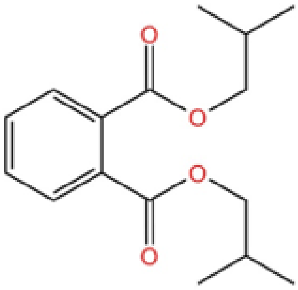
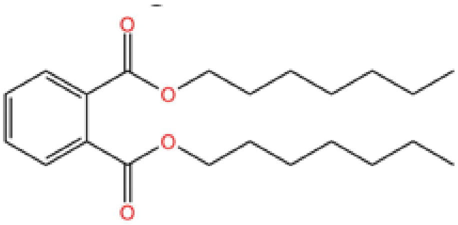
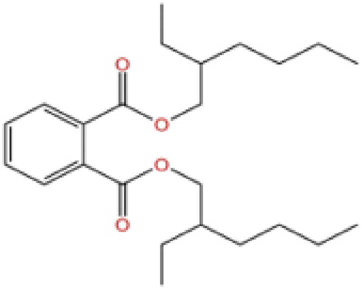
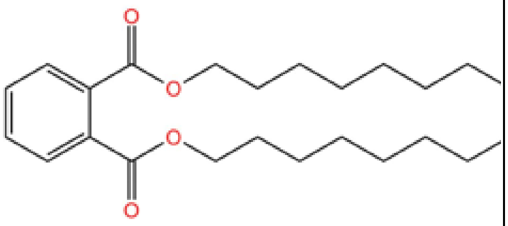
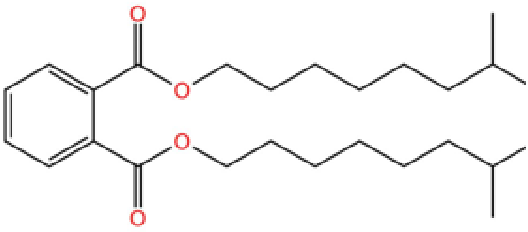
 Dibutyl phthalate (DBP)	 Diisobutyl phthalate (DIBP)
 Diisoheptyl phthalate (DIHP)	 Bis(2-ethylhexyl) phthalate (DEHP)
 Di-n-octylphthalate (DNOP)	 Diisononyl Phthalate (DINP)

Figure 5: Historically relevant phthalate plastizicers

2.2.2 Toxicity and recycling

The phthalates plasticizers are non-covalently bound to the polymeric matrix, which allows their leaching into the environment. This has resulted in the detection of phthalates in dairy and meat foods, environmental resources such as sediments and water bodies. The major routes of human exposure are dermal absorption, ingestion of contaminated food or water, and inhalation.[20,21]

Several studies about the toxic effects of DEHP on rodent physiological systems classified the chemicals as endocrine disruptors and reprotoxic. [21,22] Consequently, DEHP, Dibutyl phthalate (DBP), Benzyl butyl phthalate (BeBP) and Diisobutyl phthalate (DIBP) considered toxic substances by Regulation (EC) N°. 1907/2006. In the regulation EU Nº 143/2011 the phthalates were included into Annex XIV to REACH to regulate the adequately use. The last reform proposed restricts the marketing of articles with a phthalate concentration equal to or greater than 0.1 wt%. [23]

3. Revalorisation of legacy phthalate plasticizers

3.1. Hydrogenation of phthalate esters

As a result of the health and toxicity problems caused by phthalates, alternative plasticizers have been developed by companies. Cyclohexane diesters have been proposed as the main alternative thanks to their advanced physical properties and lower toxicity.[24] The production pathway is based on the ring-hydrogenation of the corresponding phthalate esters over noble metal catalysts or high loaded Nickel systems. A study by D-H. Phan-Vu and C-S. Tan have developed a rhodium-nickel bimetallic aiming to improve the catalyst efficiency as Rhodium, firstly breaks the conjugated ring structure, while and nickel further hydrogenates the formed intermediates.[24] Recently, an upcycling strategy for real post-consumer plastic-extracted phthalate plasticizers was developed based on a coupled (trans)esterification-hydrogenation using supported Ru-catalysts in combination with catalytic amounts of sulfuric acid. This is the first work in which end-of-life phthalates are revalorized into safe and reusable compounds. The reaction it is showed in the picture 6.[25]

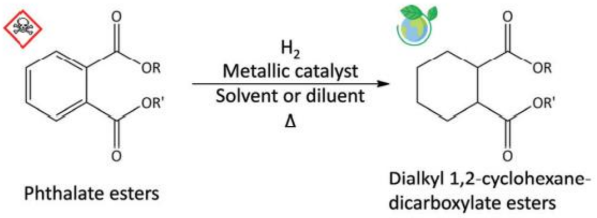


Figure 6: Chemical detoxification of phthalate plasticizers by catalytic ring hydrogenation[25]

3.2 Oxidative coupling

Oxidative coupling of aryls in the presence of a metal catalyst is one of the main routes for the formation of carbon-carbon bonds by electrophilic aromatic substitution using O_2 such as oxidant. The reaction of interest for this report involves the coupling of dimethyl phthalate (DMP) at the 4-position to give 3,3',4,4'-biphenyltetracarboxylic tetraester (S-BPTT) and 2,3,3',4'-biphenyltetracarboxylic tetraesters (A-BPTT).[26,27] Controlling the regioselectivity is of paramount importance given that only the symmetrical product (S-BPTT) is industrially relevant according that the possibility to be transformed into polyimide resins that have a high thermal stability.[27]

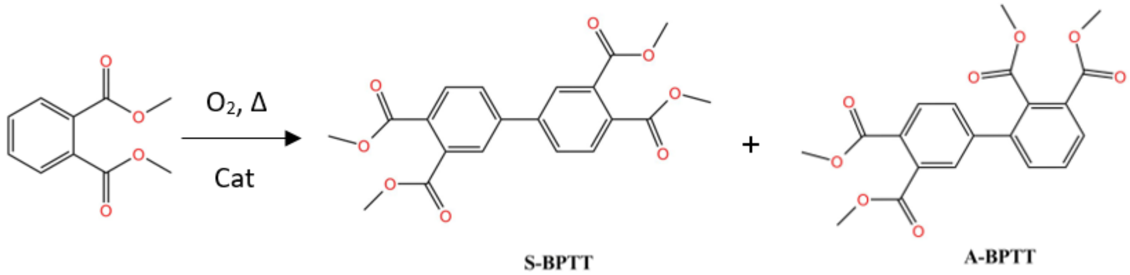


Figure 7: Reaction of oxidative coupling of dimethyl phthtalate

Homogeneous palladium (Pd) systems are often used as catalysts, in which palladium shifts between the (II) and (0) oxidation states during the catalytic cycle. The activation of the C-H bond is the rate limitating step and is determined by a concerted metalation-deprotonation (CMD).[28] A problematic issue is the deactivation of the catalyst as Pd(0) aggregates to inactive Pd black clusters. Additionally, palladium coordinates with the methoxycarbonyl group accelerating the electrophilic attack at position 3, mainly producing the undesired A-BPTT. [26] For that purpose, heterogeneous recyclable Pd catalysts in metal organic frameworks (MOFs) based on the use of solid catalysts with single-atom active sites have been developed.[29]

An interesting alternative pathway for the oxidative coupling of DMP is based on supported gold nanoparticles. In contrast to Pd-based systems, the Au-catalyzed coupling does not require additional ligands as the regioselectivity appears to be determined by steric hindrance, partially created by the Au-nanoparticles themselves. Ishida et al. developed a fairly active Au/Co_3O_4 catalyst (conversion 49%), employed in AcOH, which assured an excellent regioselectivity (94%) of the coupling reaction (1 mmol DMP, 4 mol% Au/Co_3O_4, 0.5 ml AcOH, 15 bar O2 at 150 °C for 18 h.). The reaction mechanism that has been proposed is depicted in Figure 9.[26]

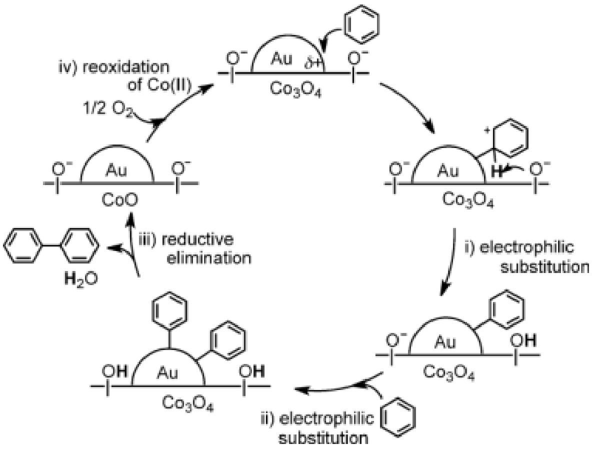


Figure 8: A possible reaction mechanism for the oxidative coupling of aromatic compounds over Au/Co_3O_4[26]

Materials and methods

1. Materials

All chemicals were used as received, unless otherwise specified: Dimethyl phthalate (Alfa Aesar, 99%), Dibutyl phthalate (J&K Scientific, 99%), Diisobutyl phthalate (TCI Europe, > 98 %), Benzyl butyl phthalate (TCI Europe, > 97%), Bis(2-ethylhexyl) phthalate (J&K Scientific ,99%), Diisononyl phthalate (TCI Europe, purity not specified), Monobutyl phthalate (TCI Europe, >95%), Phthalic acid (Thermo Fischer Scientific, 99%), Phthalic anhydride (Fischer Scientific, >99%), *n*-Dodecane (Sigma-Aldrich, >99%), Chloroform (Fischer Scientific, >99.8%), Acetic acid (Fischer Scientific, Glacial; >99%), Pivalic acid (TCI Europe, >99%), Dimethyl sulfoxide (Fischer Scientific, >99.9 %), Sulfolane (TCI Europe, 98%), *tert*-Amyl alcohol (TCI Europe, >99%), *tert*-Butanol (Sigma-Aldrich, >99%), Acetonitrile (Acros Organics, 99.5%), *N,N*-Dimethylacetamide (Sigma-Aldrich, >99%), Decane (Carl Roth, >99%), Mesitylene (Acros Organics, 97%), Propylene carbonate (Sigma-Aldrich, >99%), Butyl butyrate (Acros Organics, 98%), *gamma*-Valerolactone (Acros Organics, 98%), 1,2-Dichloroethane (Acros Organics, 99.5% Extra dry), 1,4-Dichlorobenzene (Fischer Scientific, 98%), Trifluorotoluene (J&K Scientific, 99%), Trifluoroacetic acid (Fischer Scientific, 99,9%), Cupric(II) trifluoromethanesulfonate (Sigma-Aldrich, 98%), Dimethyl adipate (Alfa Aesar, 99%), Poly(vinyl chloride) (Sigma-Aldrich, average MW ~43.000, average MN ~22,000), Gold(III) acetate (Alfa Aesar, 99.9% metal basis), Tetrachloroauric acid trihydrate (Sigma-Aldrich, ACS reagent, ≥ 49% Au basis), Urea (Sigma-Aldrich, ReagentPlus®, >99.5%, pellets), TiO_2 (Sigma-Aldrich, Rutile 99.5% trace metal basis), TiO_2 (Sigma-Aldrich, Aeroxide © P25), ZrO_2 (Alfa Aesar, 1/8" pellets). MgO (Carl Roth, > 98%), $CaTiO_3$ (Thermo Scientific, >99%), $BaTiO_3$ (Thermo Scientific, >99%).Commercial catalysts include 1 wt% Au/TiO_2 (AUROlite^{TM}, Strem Chemicals) and 1 wt% Au/ZnO (AUROlite^{TM}, Strem Chemicals).

2. Catalyst preparation

In addition to commercially available catalysts, several supported Au-systems were synthesized by the deposition-precipitation method using urea as the precipitation agent.[30,31] To that end, an aqueous solution of 4.2 x 10^{-3} M Au was prepared, employing $HAuCL_4.3H_2O$ as metal precursor. Based on the final metal loading of the catalysts (0.5 – 8 wt% Au), a given volume of the aqueous gold solution was mixed with urea (molar ratio Au:Urea 1:100) and with the required amount of the catalyst support. The glass container was then sealed, shielded from light, heated to 80 °C and stirred at 500 rpm for 18h. After Au-deposition, the solids were three times washed with deionized water, centrifuged and then dried at 60 °C for 18h. Finally, the dry materials were activated by calcination in air at 300 °C (4h, 3°C min^{-1}).

3. Catalytic reactions

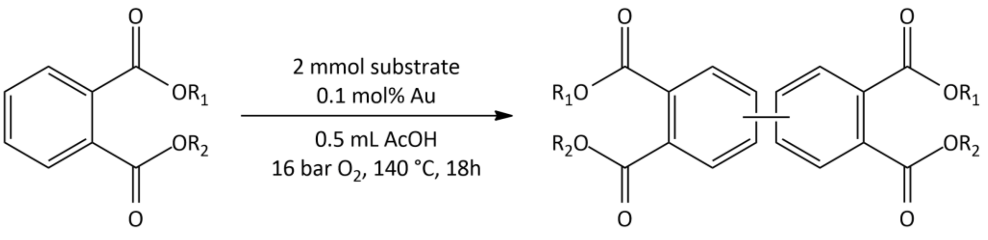


Figure 9: Reaction and conditions of the oxidative coupling of phthalate esters

In a typical reaction, a glass liner (5.5 mL) was charged with the phthalic acid derivative (2 mmol), acetic acid (0.5 mL), the heterogeneous Au-catalyst (metal/substrate 0.1 mol%) and a magnetic stirring bar. The glass vial was then partially closed using a Teflon stopper and placed in a homemade, stainless steel autoclave (11 mL). The reactor was sealed, purged three times with O_2 and pressurized with 16 bar O_2 at room temperature. Subsequently, the autoclave was placed in a pre-heated aluminum block at 140 °C for 18 hours under continuous stirring (750 rpm). The oxidative coupling reaction was stopped by fast cooling of the reactor in an ice bath and by evacuating the remaining gas at room temperature. In order to fully solubilize all products, 1 – 5 mL of chloroform was added to the mixture, after which the Au-catalyst was removed from the liquid mixture by centrifugation. With the intention of ensuring safe handling at all times, it is strongly advised to complete a thorough safety analysis prior to applying such hazardous reactions conditions. Furthermore, these experiments should only be performed in proper reactor apparatus, preferentially equipped with burst discs.

4. Product analysis and identification

The synthesis of tetraalkyl biphenyl tetracarboxylate esters by the oxidative coupling of phthalate esters was evaluated by gas chromatography (GC) and by gas chromatography – mass spectrometry (GC-MS).

GC-samples were prepared by adding 50 µL of *n*-dodecane (internal standard) to the crude reaction mixture and were subsequently injected on a Shimadzu GC-2010 instrument, equipped with a 60 m CP-Sil5 CB column and a flame ionization detector (FID). Products were identified using an Agilent 6890 GC instrument equipped with a 30 m HP-1 MS UI column and a 5973 MSD mass spectrometer.

The turnover numbers are defined as TON = 2 x mol biaryls / mol Au, the chemoselectivity represents the share of tetraalkyl biphenyl tetracarboxylate esters relative to all formed products and the regioselectivity is defined as the relative amount of 3,3’,4,4’ tetraalkyl biphenyl tetracarboxylate esters to all three biaryls.

Results and discussion

1. Temperature screening

In a first set of experiments, the effect of the reaction temperature on the oxidative coupling of dimethyl phthalate was evaluated (Figure 10). To that end, 10 mmol of DMP and 0.02 mmol of 1 wt% Au/TiO_2 (AUROlite TM, STREM) were loaded in home-made autoclaves and placed under 16 bar O_2 for 18 hours. The evaluated temperatures were 80°C, 100°C, 120°C, 140°C and 160°C. The obtained conversion is presented in terms of turn over numbers (TON) and since that 3,3',4,4'-biphenyltetracarboxylic tetramethylester (3,3',4,4'; the product of interest) is not the only product formed, the side-product formation is further evaluated in terms of regio- and chemoselectivity. While there is virtually no conversion of DMP at 80°C, a gradual increase in product formation is observed with increasing temperature yielding an active system at 140 °C (34 TON) and especially at 160 °C (70 TON). Concerning the selectivity of the reaction, it is remarkable that there does not appears to be a clear trend with the reaction temperature; Across the screened temperatures, about 58% of the coupled products present the favourable 3,3',4,4'-confirmation (regioselectivity) and phthalic acid represents one-third of the formed products. Blanc experiments at 140 °C and 160 °C (not shown), provided further insight into the role of the Au-catalyst as no coupled products were observed. Furthermore, the hydrolysis of DMP to phthalic acid even appears to be suppressed by the catalyst, however, this might also be explained by a strong adsorption of the acid compound on the catalyst. Although the experiments at 160 °C resulted in the most active coupling system (70 TON), the experiments were continued at 140 °C for selectivity (radical degradation reactions) and safety (explosion hazard) reasons.

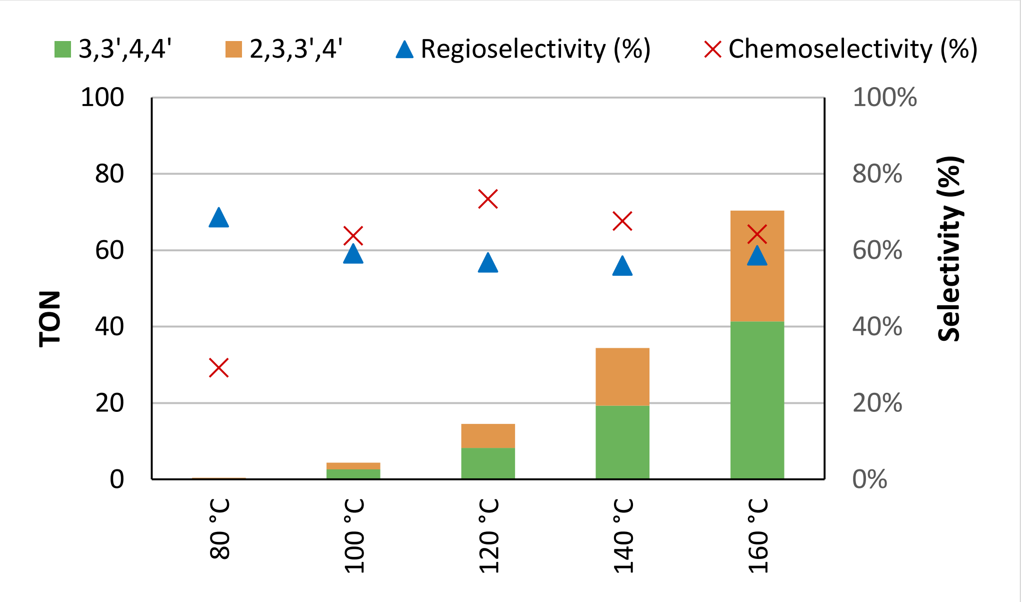


Figure 10: Temperature screening for the oxidative coupling of DMP. Reaction conditions: DMP (10 mmol), 0.02mol% Au/TiO_2 (AUROlite TM, STREM), 16 bar O_2 for 18h

2. Effect of the oxygen pressure

The oxidative coupling was carried out under different oxygen pressures (0 – 16 bar) in order to examine the effect of molecular oxygen in the system (Figure 11). From the results obtained it seems indisputable that an increased oxygen pressure is beneficial in this type of reaction, yet some aspects merit a more detailed discussion. First of all, it is remarkable that in the absence of O_2 (N_2 atmosphere), the Au-catalyst is able to perform the oxidative coupling cycle only once (TON 1), which supports the idea that oxygen *in situ* reactivates the gold system for a next cycle. On the other hand, the deficit of oxygen seems tremendously beneficial for the regioselectivity as almost exclusively the desired biphenyl isomer was formed (91% regioselectivity to 3,3',4,4'). Nevertheless, the chemoselectivity plummeted (10%) due to the catalyst-independent formation of the phthalic acid, which remained constant over the different oxygen pressures. Increasing the oxygen pressure results on the one hand in an upward trend of TONs, which also considerably improves the chemoselectivity to 68% at 16 bar O_2. On the other hand, the regioselectivity initially drops sharply, after which it stabilizes to the point where ±6 out of 10 couplings results in the symmetrical biphenyl compound (3,3',4,4'). For further parameter optimization, the applied pressure was maintained at 16 bar O_2 in order to perform the evaluations under a clearly active system.

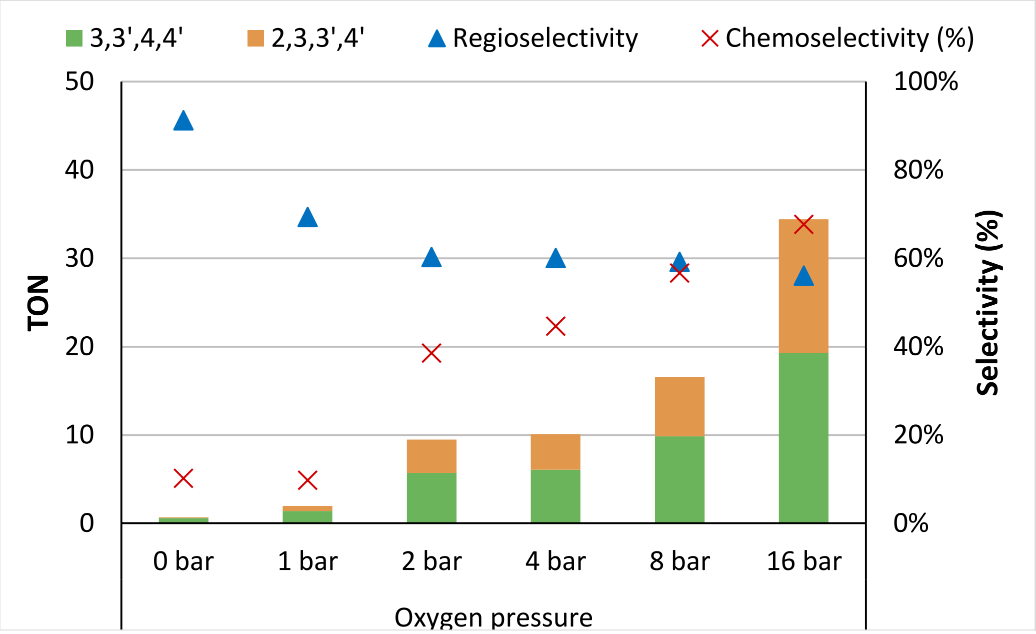


Figure 11: Oxygen pressure screening for the oxidative coupling of DMP. Reaction conditions: DMP (10 mmol), 0.02mol% Au/TiO_2 (AUROlite TM, STREM), 140°C for 18h

3. Time profile

Subsequently, the effect of time on the product distribution and yield was evaluated (Figure 12), as the idea arose that the catalyst may get deactivated over time. Nevertheless, it appears that no deactivation of the catalyst seems to take place within the first 18 h of reaction time, but instead the oxidative coupling over heterogeneous Au-catalysts is a rather slow reaction. It is also remarkable that the regioselectivity is constant over time, but that the share of phthalic acid in the product distribution rapidly decreases from 66% to ±30%, after which it seemingly remains constant. Further optimisation was performed with 18 h of reaction time, although longer times would be interesting to study the catalytic system at higher phthalate conversions.

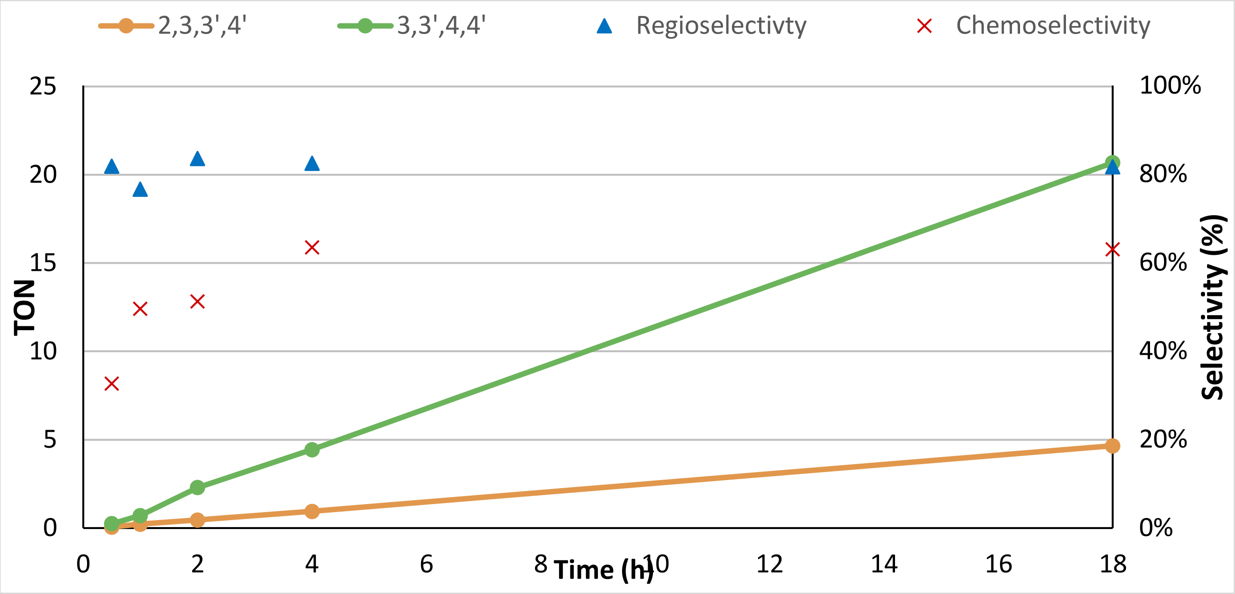


Figure 12: Time profile for the oxidative coupling of DMP. Reaction conditions: DMP (2 mmol), 0.1mol% Au/TiO_2 (AUROlite TM, STREM), 140°C and 16 bar O_2

4. Solvent influence

4.1 Solvent screening

In an attempt to boost the phthalate conversion (from <5% under solventless conditions) to higher values, numerous solvents were screened for the oxidative coupling of DMP (2 mmol DMP in 0.5 mL solvent; Figure 13). From the extensive solvent screening it could be concluded that the oxidative coupling of phthalates does not happen in whatever organic medium, as 8 out of 16 solvents completely prevented the reaction. In only three evaluated solvents -acetic acid (AcOH), sulfolane and mesitylene- a TON greater that 5 was achieved, furthermore, the catalyst showed in all solvents a lower coupling activity compared to the solventless system. Nevertheless, the reaction in AcOH appears to be promising as a remarkably improvement in regioselectivity was observed (> 80%), resulting in an approximately constant TON (11 $TON_{3,3',4,4'}$) towards the more valuable 3,3',4,4'-isomer in comparison to the solventless system (13 $TON_{3,3',4,4'}$). For the same reason the effect of acetic acid on the reaction will be further investigated in subsequent experiments.

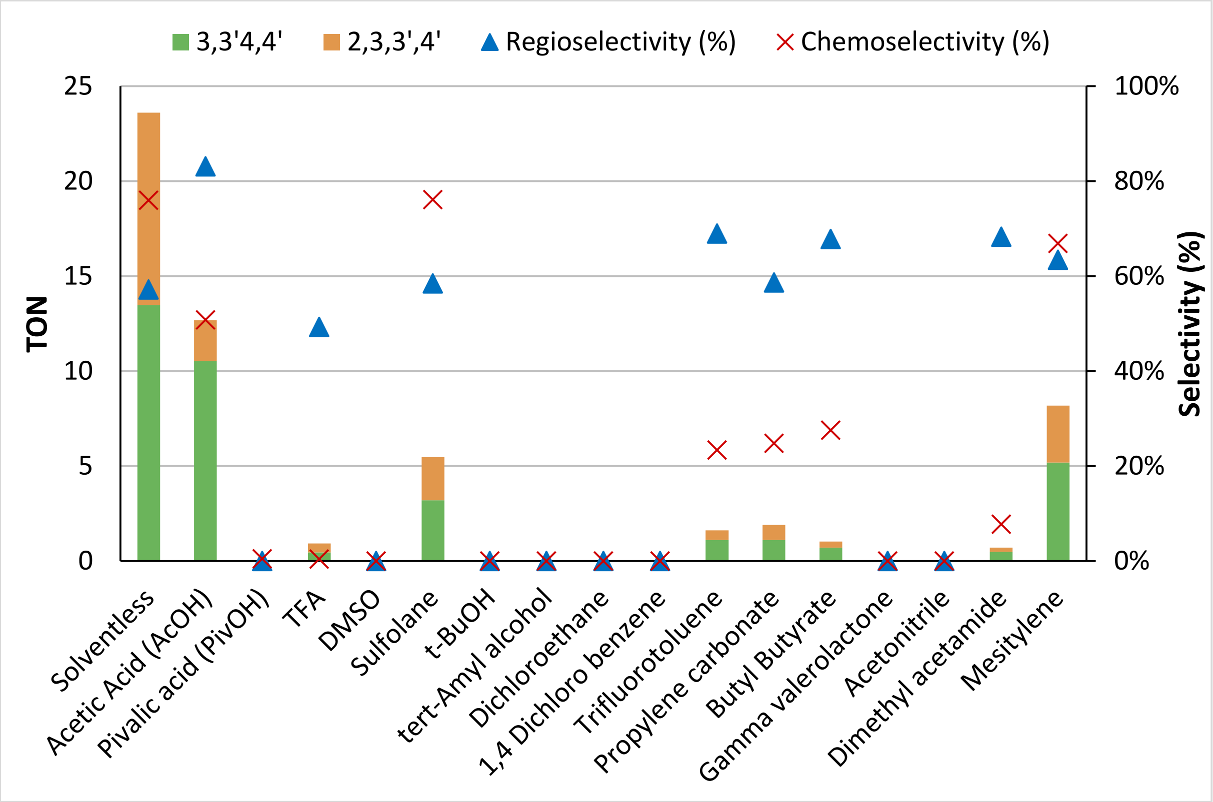


Figure 13: Solvent screening for the oxidative coupling of DMP. Reaction conditions: DMP (2 mmol), 0.1mol% Au/TiO$_2$ (AUROlite TM, STREM), defined solvent (x mL), 140°C, 16 bar O$_2$ for 18h

4.2 Acetic acid concentration

From the solvent screening, it was evident that only acetic acid might be beneficial for this oxidative coupling. In order to further evaluate the effect of acetic acid concentration (figure 14), a set of experiments was carried out with different amount of the solvent (0 – 2000 µL). The results clearly show that the activity of the Au-catalyst for the oxidative coupling of DMP initially increases when small quantities of AcOH are added, but drops again when an excess of the solvent is added, reaching a maximum at 62.5 µL AcOH (47 TON). On the other hand, a steady increase in regioselectivity (up to 84% at 2 mL AcOH) is observed at increasing AcOH concententration. Nevertheless, the substantial improvements are observed at low amounts of AcOH, given that already 76% regioselectivity is obtained by adding only 67.5 µL AcOH compared to 57% in the solventless system. Noteworthy is the decreasing trend in chemoselectivity for high AcOH amounts, which can mainly be explained by the reduced biaryl yield as the phthalic acid production remains rather constant, thereby increasing its relative share in the obtained products. For follow-up experiments, 0.5 mL of AcOH was employed to further highlight differences in coupling activity between sever systems.

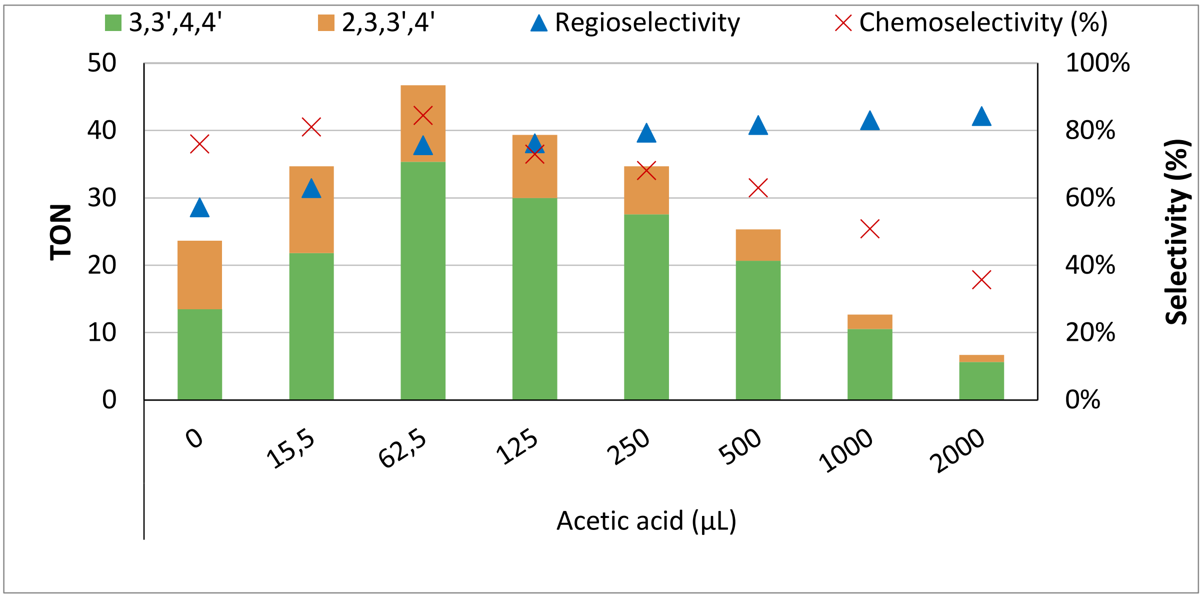


Figure 14: Effect of the added amount of acetic acid concentration in the oxidative coupling of DMP. Reaction conditions: DMP (2 mmol), 0.1mol% Au/TiO_2 (AUROlite TM, STREM), AcOH (defined volume), 140°C, 16 bar O_2 for 18h

4.3 H_2O influence

Given that water in the reaction system is presumably responsible for the side-product formation of phthalic acid, the effect of the water content on the oxidative coupling reaction was subsequently investigated (Figure 15). The obtained results seem to support the previous hypothesis as the amount of phthalic acid gradually increases with the water content (not explicitly shown, derivable from chemoselectivity). At the same time, the formation of the biaryl productsdecreases gradually with the water increase, further reducing the chemoselectivity. It is, however, remarkable that the regioselectivity remains relatively constant. It is hypothesized that part of the water molecules and/or phthalic acid competitively adsorb on the Au nanoparticles, decreasing the rate of the oxidative coupling of phthalate esters. In any case, the amount of water in the reaction medium should be avoided as much as possible.

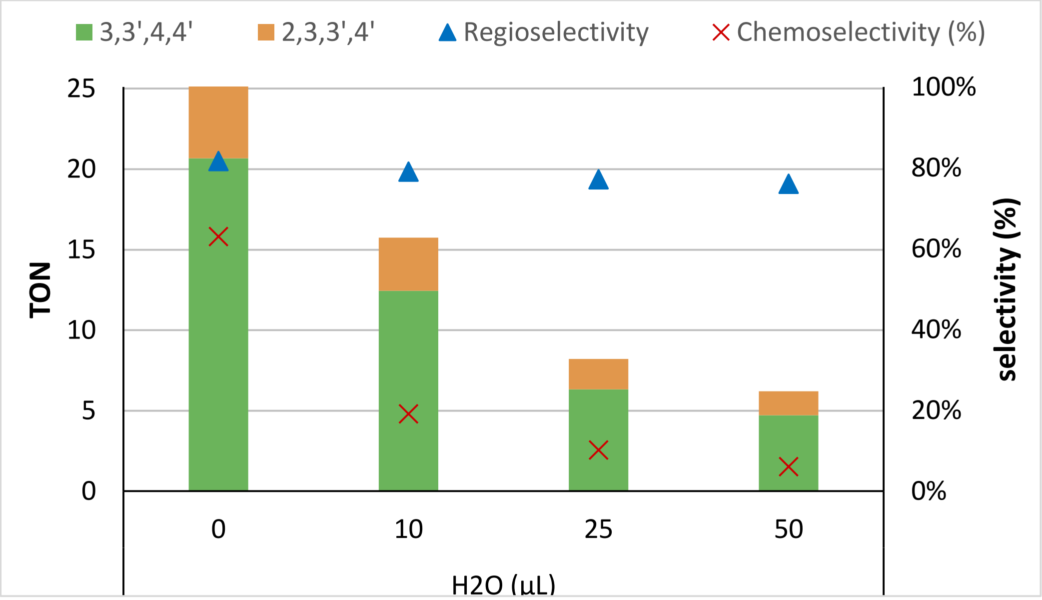


Figure 15: The effect of water on the oxidative coupling of DMP. Reaction conditions: DMP (2mmol) in AcOH (0.5mL), 0.1mol% Au/TiO_2 (AUROlite TM, STREM), water (defined amount added, 140°C, 16 bar O_2 for 18h

5. Effect of the chosen catalyst

5.1 Catalyst activation screening

In this set of experiments, from two catalysts various types of activations were applied to determine their influence on the oxidative coupling of DMP (Figure 16). The catalyst tested were 1wt% Au/TiO_2 (AUROlite TM, STREM) and 1wt% Au/TiO_2 (Rutile). The activation method of AUROlite has little impact on the catalytic activity. Nevertheless, when rutile is used there is hardly any DMP conversion in non-activated compound, in the H_2 activated compound there is a slight product formation. Activation by calcination produces a higher reaction yield (17.7 TON), even though it is inferior compared with the activity from AUROlite (20.69 TON). Uses a O_2 atmosphere to activate the catalyst consolidate the catalyst mechanism idea. The effect of the catalyst has not been covered fully, forthcoming experiments will investigate other relevant parameters.

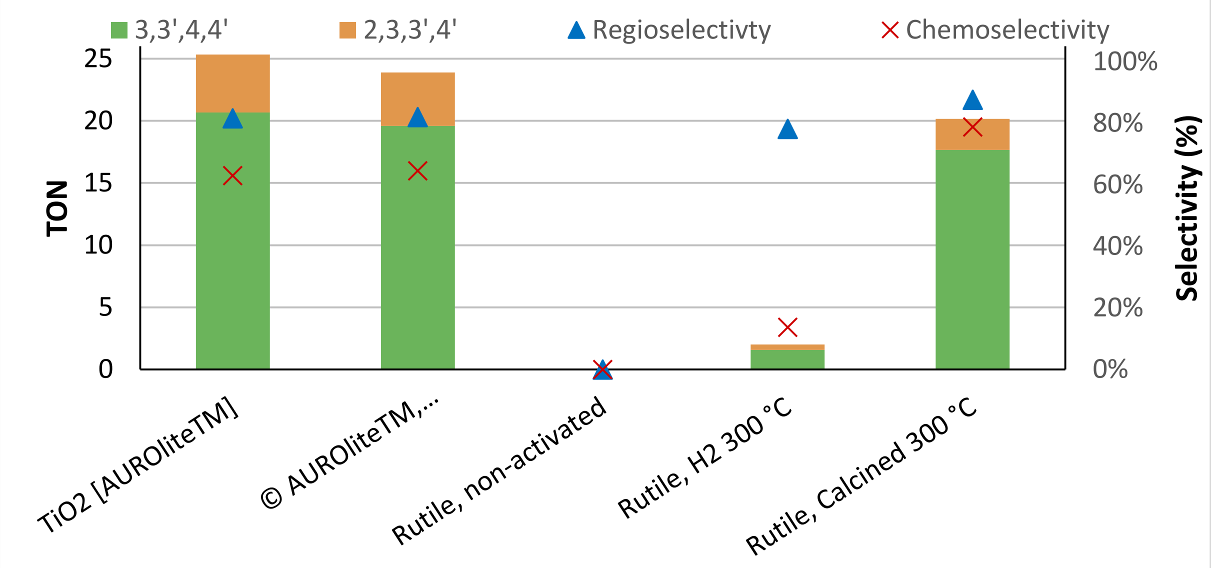


Figure 16: Catalyst activation for the oxidative coupling of DMP. Reaction conditions: DMP (2mmol) in AcOH (0.5mL), 0.1mol% Au/TiO_2, 140°C, 16 bar O_2 for 18h

5.2 Effect of the gold loading

Given that the metal particle size appears to be crucial within heterogeneous gold catalysis, the metal loading on the Au/TiO_2 catalyst was varied in this set of experiments (Figure 17). Nevertheless, the obtained results suggest that the metal loading has little or no effect on the TON, regio- and chemoselectivity. Remark that the amount of gold in the reaction remained unchanged through the whole set of reactions. This effect is probably the result of the chosen catalyst preparation method, as the urea deposition strategy is specifically used to obtain catalysts with a constant metal particle size, independent of the chosen loading (< 8 wt%). Verification of this hypothesis is beyond the scope of this work, however, it is strongly recommended to investigate the various catalysts by TEM.[32] Increasing the metal loading might be useful to raise the amount of Au in the system without creating a too viscous slurry due to too high solid content (i.e. catalyst particles).

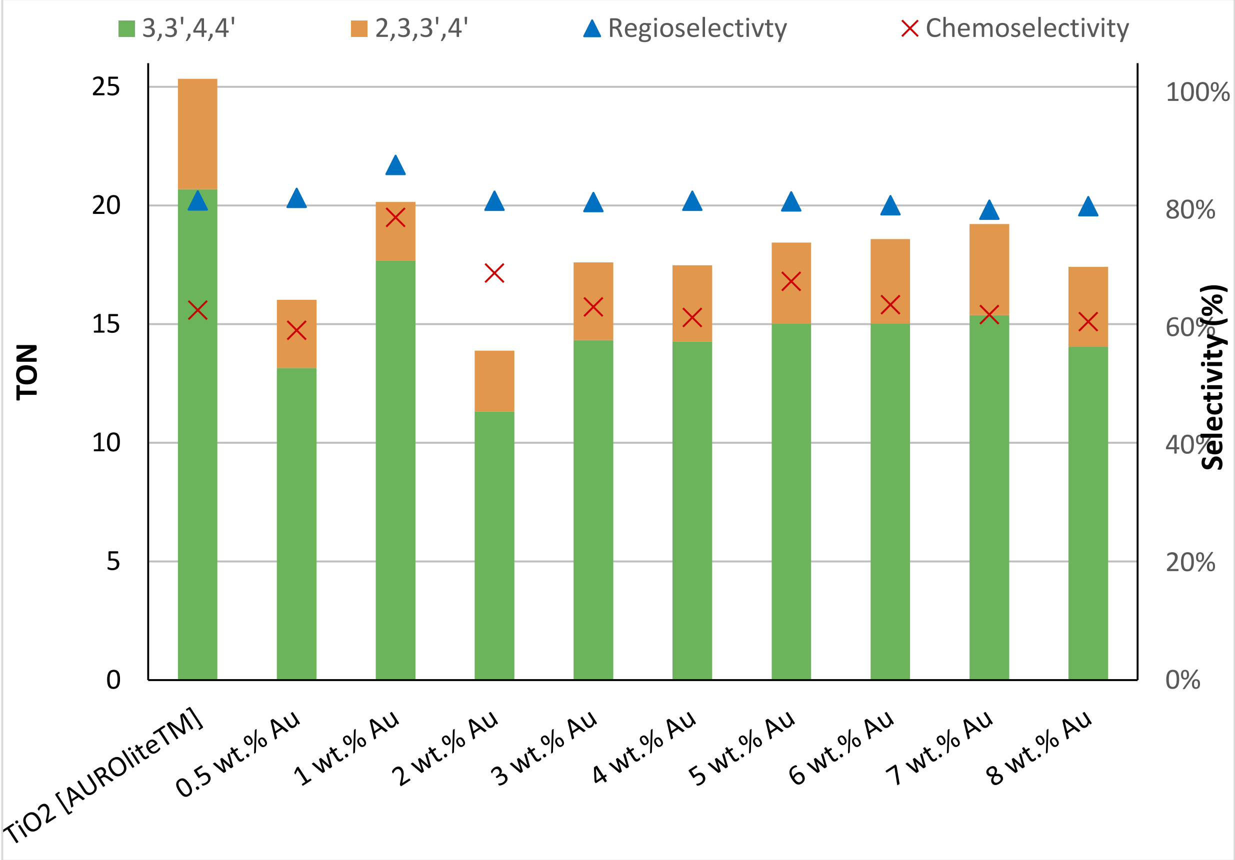


Figure 17: The effect of the gold loading of the catalyst on the oxidative coupling of DMP. Reaction conditions: DMP (2mmol) in AcOH (0.5mL), 0.1mol% Au/TiO_2, 140°C, 16 bar O_2 for 18h

5.3 Catalyst support screening

The last parameter to be evaluated in this dissertation is the catalyst support (figure 18). Despite the relatively extensive support screening, it proved exceptional to synthesize a more effective system for the oxidative coupling of phthalate esters than the commercial Au/TiO_2. However, systems based on for example TiO_2[rutile], $CaAl_2O_4$, $MgAl_2O_4$ and $CaTiO_4$ showed an increased regio-and chemoselectivity, which is equally desirable given that phthalic acid and A-BPTT can be considered as waste. Without any doubt the ZrO_2 system can be referred to as the most promising catalyst, as it combines the highest observed coupling activity (TON 34) with one the highest regio- and chemoselectivity (> 80 %).

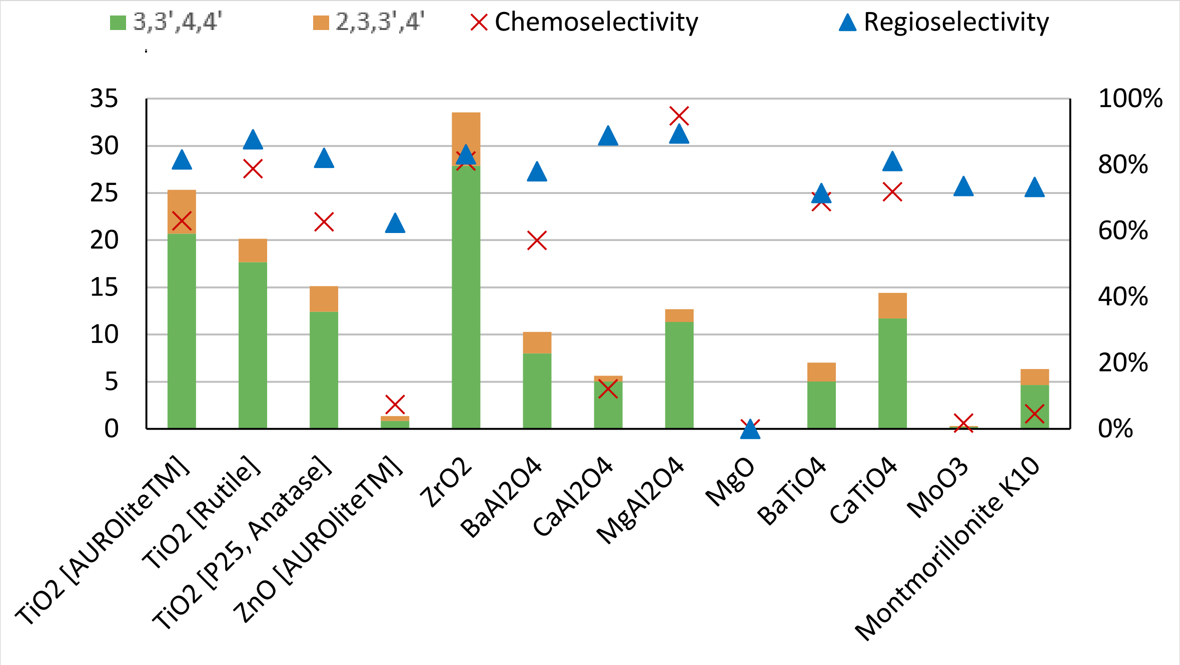


Figure 18: Catalyst support screening for the oxidative coupling of DMP. Reaction conditions: DMP in AcOH (2 mmol; 0.5mL), 0.1mol% Au/TiO2, 140°C, 16 bar O_2 for 18h

Conclusion

The catalytic revalorisation of dialkyl phthalates, via oxidative coupling reactions using supported Au catalysts and O_2 as the atom-efficient oxidant under ligand-free conditions has been investigated in this dissertation. Increased reaction temperatures (≥ 120 °C) proved necessary to activate the Au-catalyst for the oxidative coupling and the oxygen atmosphere allowed to perform the catalytic cycle multiple times by reoxidizing the gold nanoparticles. Several solvents were tested, however, only acetic acid proved relevant, as the compound substantially improved the regio-selectivity of the coupling reaction. Furthermore, changing the added amount of the solvent gave rise to a more selective and more active system compared to the solventless variant. Finally, the Au-catalyst itself was investigated, in which the commercial Au/TiO_2 served as a reference to allow a straightforward comparison. Firstly, the effect of the gold loading was evaluated, however, quite constant TONs and selectivities were obtained in the range of 0.5 – 8 wt% Au. It is hypothesized that the catalyst synthesis method (urea deposition followed by calcination) gives rise to metal particles of the same size regardless of the metal loading. In terms of activity, it proved rather challenging to surpass the commercial AUROlite. Nevertheless, from an extensive support screening a Au/ZrO_2-catalyst eventually exhibited the highest coupling activity and even combined it with an excellent regioselectivity for the desired product.

To conclude, the optimal conditions for the oxidative coupling of phthalates are 2 mmol of DMP in AcOH withf 1wt% Au/ZrO_2 as catalyst, under 16 bar O_2 at 14 0^oC for 18 hours. While further increasing the oxygen pressure and/or reaction temperature will increase the obtained yields, it is considered too dangerous. On the other hand, increasing the amount of gold in the reaction and/or reaction time can be considered as a safe way to improve the obtained yields. While further research is clearly advised, these results may already contribute to the development of a real revalorisation strategy for end-of-life PVC extracted phthalate esters. The next step after this research is evaluate the effect of residual PVC in the reaction simulating the process in an end-of-life extract. It also opens the oxidative coupling analysis of other phthalates such DEHP which has importance in the plastic industry.

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