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GLYCEROL AND SUPERCRITICAL CARBON DIOXIDE: TOWARDS GREENER CATALYTIC PROCESSES

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Abstract. Here in this communication, we report that combination of glycerol with scCO₂ is a convenient tool for designing highly green catalytic processes. Indeed, as water, glycerol is cheap, abundant and non toxic. However, as compared to water, glycerol is poorly miscible and non reactive with scCO₂ offering thus an alternative of choice for overcoming a lot of drawbacks encountered with water and scCO₂

Key-words. Glycerol, scCO₂, catalysis; green process, Heck coupling

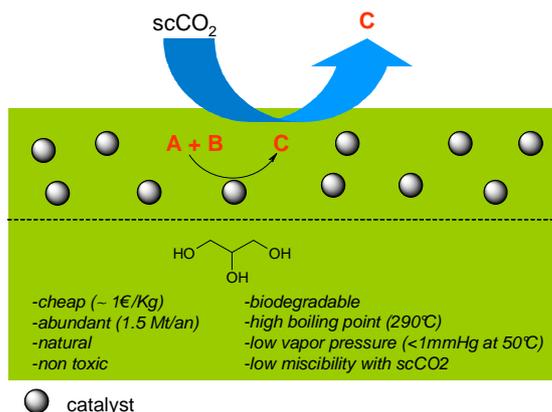
Most of organic transformations are operated in a liquid phase, and the choice of the solvent is then crucial for a good control of the progress and/or selectivity of the reaction. Indeed, the solvent allows a better contact between the reactants, stabilises or destabilises intermediates and/or transition states, but also determines the choice of work up procedures and recycling or disposal strategies. Taking now into account the impact of chemical processes on the environment, the search of innovative concepts for the substitution of volatile organic solvents in catalysis has become a tremendous challenge in academia and industry.

Among all the reported strategies, the use of water as a solvent was probably one of the most investigated solution. This tendency arises from the fact that water combines both environmental and economical benefits, which represent a prerequisite for the viable utilization of a green solvent. Fascinating reviews related to this topic can be found in the literature.¹ However, despite remarkable results were observed in/on water, development of aqueous systems is still subject to strict limitations owing to the low boiling point of water and to its harmful reactivity towards various functional organic groups and/or catalytic sites, which may lead to the formation of undesirable products. Extraction of the reaction products can be also technically difficult. Indeed, in most cases, the use of an organic solvent is unfortunately needed, which decreases the environmental benefit of using water as a green solvent^{2, 3}. With the aim of overcoming this issue, some groups investigated the possibility of extracting the products of the reaction from water using supercritical carbon dioxide (scCO₂)⁴. Compared to the conventional extraction with organic solvents, this route indisputably offers environmentally friendlier processes. However, combination of water as media for catalysis with scCO₂ as the extracting solvent is strongly limited by (i) the non negligible solubility of water in scCO₂ and (ii) the side formation of carbonic acid which requires a close pH control of the aqueous phase (which can be achieved by addition of buffering salts)⁵.

As an alternative to water, many investigations were also directed towards the use of ionic liquids (ILs). These approaches were smartly based on the fact that ILs exhibit high boiling points and are poorly soluble in scCO₂, offering a promising solution for (i) a cleaner extraction of the reaction products and (ii) an easier recycling of the catalyst. However, hazardous toxicities and relatively high prices of ILs are up to now the main limitation to their development⁶. It should be noted that the use of polyethylene glycol (PEG) as solvent for catalysis appears today as a good compromise between water and ILs. Indeed, PEG is much less toxic and far cheaper than ionic liquids and, according to its average molecular weight, PEG can be poorly soluble in scCO₂⁷.

On the continuation of our work, we wish to show here that glycerol may offer some remarkable advantages over water, allowing us to overcome a lot of drawbacks encountered with the system water-scCO₂. Glycerol is poorly soluble in scCO₂, chemically inert towards CO₂ in standard conditions (no pH

control is required), exhibits a high boiling point (290°C) and a low vapour pressure (< 1 mmHg at 50°C)



Scheme 1: Glycerol/scCO₂ system

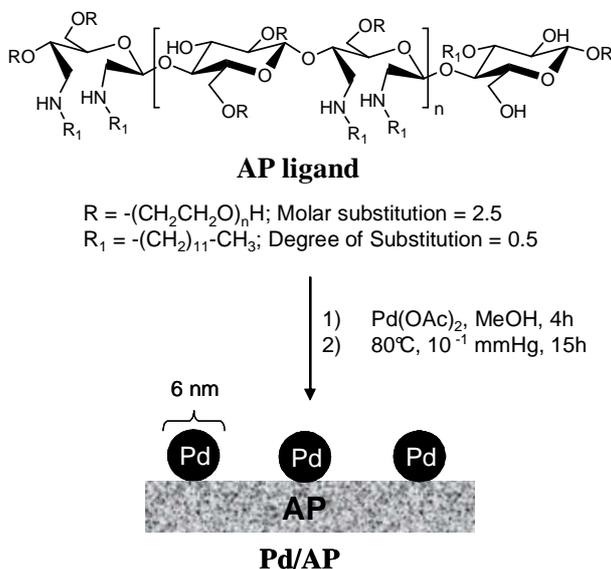
Moreover, the design of catalysts, able to promote organic reactions in glycerol, nearly obeys the same rules than those of catalysis in water. Like water, we recently distinguished two types of catalysis (i) *catalysis on glycerol* where glycerol has a beneficial effect on the reaction rate of various organic transformations and (ii) *catalysis in glycerol* where the intrinsic reactivity of glycerol as well as the low solubility of organic substrates was successfully overcome owing to the formation of catalytic hydrophobic pockets.

1. CATALYSIS IN GLYCEROL

For the demonstration of our concept, we investigated the catalytic Heck coupling in glycerol. This reaction is of fundamental importance in organic chemistry and has broad applications from the manufacture of basic chemicals to the preparation of fine pharmaceuticals making of this reaction a suitable model reaction for our investigations.

In a first set of experiments, we investigated the catalytic coupling of iodobenzene with cyclohexylacrylate in glycerol, yielding the corresponding (*E*)-cyclohexyl cinnamate. In order to overcome the low solubility of organic reactants in glycerol we explored the possibility of using an amphiphilic aminopolysaccharide (AP) as a ligand for the coordination of palladium. Indeed, owing to its amphiphilic structure, we recently reported that this AP was able to emulsify a glycerol-based medium leading to a dramatic improvement of the reaction rate.

AP was synthesized according to our previous method using hydroxyethylcellulose and dodecylamine as starting raw materials⁸. Coordination of palladium on AP was performed as follow. In a typical procedure, the AP ligand (100 mg) was first dissolved in 5mL of methanol and then added to 10mL of a methanolic solution of Pd(OAc)₂ (0.3 g/L). The solution was mixed for 4 hours and the methanol was then gently removed under reduced pressure. The recovered black solid was placed in an oven for 15h at 80°C and 10⁻¹ mmHg leading to the corresponding surfactant-combined-catalyst named Pd/AP. ICP analysis revealed a Pd content of 1,38 wt%.



Scheme 2: Stabilization of Pd nanoparticles on AP

making easier and safer the development of catalytic processes at temperature higher than 100°C. Even if the solubility of glycerol in scCO₂ is slightly higher than that of ILs, we designed here a convenient pathway combining (i) catalysis in a cheap and sustainable medium and (ii) a clean extraction of the product of the reaction with scCO₂.

Recently, we reported that the use of glycerol as a solvent presents some close similarities with water. This led us to familiarly termed glycerol as “organic water” in the literature.⁸ Indeed, like

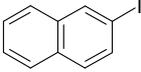
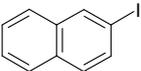
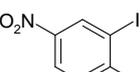
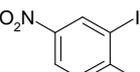
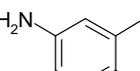
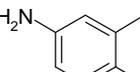
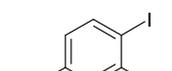
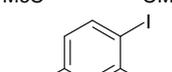
water, glycerol is highly hydrophilic, non toxic, cheap (0.8€/Kg, sometimes even cheaper than water!) and abundant.

As expected, whereas commonly used palladium-based catalysts were found poorly active in glycerol, we observed that owing to its amphiphilic properties, Pd/AP afforded, after 24h of reaction at 90°C, the (*E*)-cyclohexyl cinnamate with 91% yield.

Having this catalyst in hand, we then investigated the scope of the Pd/AP catalysts using various aryl halides and acrylate derivatives. Results are summarized in table 1. Butyl- and cyclohexylacrylate derivatives were successfully coupled in glycerol with iodobenzene and the corresponding Heck adducts were obtained in the yield range of 76-91% (Table 1, entries 1-2). Interestingly, in presence of the highly hydrophobic idonaphthalene, yields were still high (70-

94%) pushing forward the great contribution of Pd/AP for conducting Heck coupling in glycerol. Logically, starting from more polar substrates, reaction rate were higher and products were isolated with 65-95% yield.

Table 1: Catalytic Heck coupling in glycerol

$\text{RO}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2 + \text{ArX} \xrightarrow[\text{glycerol / 90}^\circ\text{C}]{\text{Pd/AP (2 mol\%)} / \text{NEt}_3} \text{OR}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{Ar}$				
Entry	R	ArX	Time (H)	Yield (%) ^[a]
1	cyclohexyl		24	91
2	butyl		24	76
3	cyclohexyl		36	94
4	butyl		36	70
5	cyclohexyl		24	95
6	butyl		24	86
7 ^[b]	cyclohexyl		24	69
8 ^[c]	butyl		24	60
9 ^[b]	cyclohexyl		24	75
10 ^[c]	butyl		24	65

^[a] isolated yield; ^[b] reaction performed at 60°C, ^[c] reaction performed at 80°C

2. POST-REACTIONAL SEPARATION WITH SCCO₂

2.1 Experimental set-up

Raw mixture from the Heck-coupling into glycerol has then been separated with scCO₂ in order to investigate the possibility to achieve a selective removal of the Heck product from the mixture of solvent and catalyst.

Extraction of reaction product has been explored thanks to a supercritical fluid extraction SEPAREX SF200 pilot (Separex Company, Champigneules, France). This experimental set-up comprises an extraction vessel (200 mL) followed by a cascade of three cyclonic separators connected to the extractor. The injection device of CO₂ has been adapted to allow processing of a liquid. Indeed, the CO₂ is injected and dispersed into the liquid using a can equipped with a HPLC pump inlet filter. Specific demisting device were placed above the liquid phase to prevent from liquid droplets entrainment. The cascade of separators allows a progressive depressurization providing separation of gaseous CO₂ from extracted products, and a good recovery of extracted products in the separators. Temperatures and pressures are controlled in each unit of the pilot, pressure being limited to 30 MPa and temperature

around 333K. Temperature of the mixture in the extractor is adjusted thanks to a heating fluid circulating in the jacket of the extractor. Subcooled liquid CO₂ is pumped by a volumetric membrane pump (Milton Roy, max. 5 kg/h), then heated until the desired temperature and continuously introduced into the extractor. The operation is typically semi-continuous, since the mixture to be separated is introduced into the extractor at the beginning of the experiment and then CO₂ is continuously introduced into the extractor.

In a typical experiment, the raw reactional mixture containing glycerol, reaction product and catalyst, was placed into the extractor vessel and the temperature was adjusted to the desired value. Then supercritical CO₂ was introduced into the extractor. The flowrate of CO₂ was measured thanks to a Coriolis flowmeter. A mixture of CO₂ and solutes was then continuously flowing out of the extractor, and the solutes were isolated thanks to the cascade of separators. The extracted compounds were then collected at the separators outlets, and mixed together, each 30 minutes. In a first approach, only kinetics of global extraction has been studied by measuring the global amount of collected samples along the time (not the composition of the samples).

2.2 Experimental results

Extraction of the reaction products has been done without any idea of solubility of this compound into CO₂. Moreover, in the case of liquid mixture to be separated, it would be necessary to have a good knowledge of fluid phase equilibria of the CO₂/glycerol/products of reaction mixture in order to optimise operating conditions for a selective recovery of products of reaction.

As a consequence, results presented in this study have to be regarded as preliminary results, showing the feasibility of the extraction.

The global composition of the raw reactional mixture before scCO₂ treatment is 13.4 g of butyl 3,3-diphenylacrylate, 3.2 g of Pd/AP and 6.2 g of excess of iodobenzene. All of these are contained in 80 mL of glycerol. The main product of reaction for this Heck-coupling is the butyl 3,3-diphenylacrylate which corresponds to the entry 2 in table 1.

Conditions of extraction are given in table 2. The operating temperature has been chosen to be 323 K in order to decrease the viscosity of the mixture to be treated and the pressure has been chosen to be quite high in order to favour extraction of reaction products.

Table 2. Operating conditions of extraction

P _{extractor} (MPa)	25
T _{extractor} (K)	323
Time for extraction (min)	390
CO ₂ flowrate (g.min ⁻¹)	15

Preliminary results of extraction are presented on figure 1 in terms of instantaneous and cumulated mass of collected samples at the outlet of the 3 separators during the extraction.

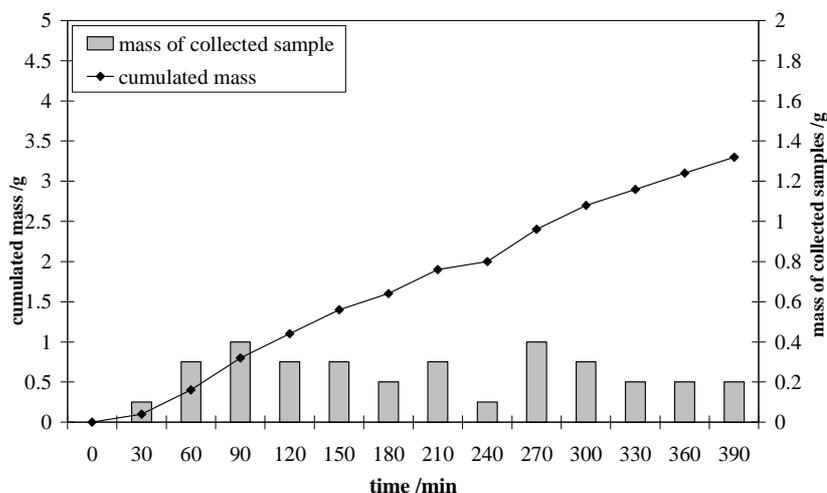


Figure 1: Extraction of the reaction products from glycerol using the scCO₂ technology.

We observe from figure 1 that extraction of the reaction products is not finished after 390 min of processing, since amount of extracted collected product at fixed intervals of time of 30 minutes is almost constant during all the experiment.

Final cumulated collected sample has been centrifuged in order to separate the apparent aqueous and organic phases. The organic phase represents 93 %w/w of the sample (corresponds to an extraction efficiency of 75%) (7 %w/w for the aqueous phase). After ¹H-NMR analysis the aqueous phase reveals to contain 71% of glycerol and 29% of water, while the organic phase is mostly constituted of the product of reaction, i.e. the butyl 3,3-diphenylacrylate. Finally, the extract contains 93 %w/w of product of reaction, 5%w/w of glycerol and 2% w/w of water.

Although the evolution of the composition of the extract is not known from this experiment, we can conclude that the extraction has been very selective towards the targeted product of reaction. Indeed, as expected, glycerol has been extracted in low proportion, and that is consistent with the low solubility of glycerol into CO₂. Sovová *et al.*⁹ measured solubility of glycerol into supercritical CO₂ under different conditions of pressure and temperature. Under our experimental conditions of pressure and temperature, solubility of glycerol can be estimated around 0.07.10⁻³ g of glycerol/g of CO₂. Considering the CO₂ flow rate in our experiment, the maximum amount of glycerol that could be extracted (in the hypothesis were glycerol was alone in the extractor) is equal to 0.4 g. The amount of extracted glycerol is here equal to 0.17g and this value is consistent with the fact that the solubility of glycerol into CO₂ is here minored by the presence of the product of reaction.

From our results, we can conclude that the extract mostly contains the product of reaction, whose solubility in supercritical CO₂ is important. Obviously, as it is the case in our experiment, the extraction seems to be firstly limited by the solubility of the product into CO₂, and more generally by the thermodynamic equilibrium of the ternary CO₂/product of reaction/glycerol mixture. Because we are here in the presence of a mixture, the fraction of product present in the CO₂ phase is linked to the fraction of product into the liquid phase by the thermodynamic equilibrium. As a consequence, for a longer extraction time, we will further observe a decrease of the rate of the extraction due to a decrease of the fraction of reaction product into the mixture.

Finally, the extraction yield of targeted reaction product is here equal to 42% w/w. Considering the fact that the CO₂ flowrate was quite low and that extraction was obviously far from being finished we are confident to achieve higher extraction yields in the future thanks to the scCO₂ extraction. An important step towards the success of this process will be to measure high pressure phase equilibria of the CO₂/butyl 3,3-diphenylacrylate mixture. Indeed, the choice of suitable operating conditions will be based on the knowledge of the thermodynamic behaviour of the ternary CO₂/glycerol/ butyl 3,3-diphenylacrylate system.

3. CONCLUSION

In conclusion, we reported here some preliminary data concerning the combination of glycerol with scCO₂ to develop green processes for organic syntheses. In particular, using the Heck coupling as model reaction, we showed that it was possible to design highly green catalytic process combining (i) the utilization of a cheap and sustainable media (glycerol) and (ii) a clean extraction of the product of the reaction with scCO₂. Additional studies on these aspects are topics of current investigations and possibility of performing catalytic processes in glycerol and under dense CO₂ is particularly studied.

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