

Carbon Dioxide Oversolubility in Nanoconfined Liquids for the Synthesis of Cyclic Carbonates

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Carbon Dioxide Oversolubility in Nanoconfined Liquids for the Synthesis of Cyclic Carbonates

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Abstract: *The physical phenomena of gas oversolubility in nanoconfined liquids was successfully applied for the catalytic cycloaddition of carbon dioxide to epoxides to generate organic cyclic carbonates. Hybrid adsorbents based on MCM-41 and SBA-15 mesoporous silica materials were synthesized and efficient nucleophile deposition on the surface of the support was achieved through a grafting procedure, allowing for an effective and durable metal-free catalytic system. Room temperature transformation of styrene and hexene oxides to the corresponding organic carbonates at atmospheric pressure of carbon dioxide is shown.*

The physical properties of fluids confined into nanoscopic pores or layers differ dramatically from the properties of the same fluids in the bulk.^[1] For example, gas trapped in nanometer-size pores order into crystalline arrays^[2] or condenses in the pores at lower pressure than the saturation pressure of the bulk liquid.^[3] The so-called finite-size effects are attributed to the competition between fluid–wall and fluid–fluid forces, leading to liquid reorganization and to a change in order level.^[4] Although gas solubility in liquids has been reported in the literature for more than a century, studies focusing on gas absorption in liquids at the nanoscale level remain very scarce. The solubility of a gas in a bulk solvent is conventionally described by Henry's Law. However, Pera-Titus and coworkers provided the first experimental evidence for a dramatic increase in gas solubility in solvents confined in mesoporous materials, dubbed “nanoliquids”, which led to the concepts of oversolubility and hybrid adsorbent to describe this effect.^[5] Hybrid adsorbents were defined as heterogeneous systems comprising of liquids confined into nanoporous environments where oversolubility of a gas occurs.^[6] It was further observed that the solubility of H₂ and light hydrocarbons (e.g., methane, ethane) confined in mesoporous alumina or silica increased 15 times when the nanoliquid size domain is less than 15 nm. Moreover, gas oversolubility appears to be promoted only when the gas/liquid interface is localized within the solid mesopores, that is, for solvent loadings lower than the total pore volume of the solid. A number of prospective solid supports and physical solvents were

chosen to prepare the hybrid adsorbents, and were evaluated in CO₂ adsorption experiments.^[6] As a result, high-surface-area mesoporous MCM-41 and alumina solid materials were identified as the most suitable hybrid adsorbents in the case of a CO₂-removal application. Recently, Porcheron and Pellenq performed grand canonical Monte Carlo simulations in order to interpret the CO₂ solubility behavior in a MCM-41 hybrid adsorbent. Importantly, simulated adsorption isotherms of CO₂ nicely matched the experimental data for three distinctive systems: bulk solvent, raw MCM-41, and hybrid MCM-41. These authors realized that, in fact, the presence of solvent molecules favors the layering of CO₂ molecules within the pores without its chemical activation; therefore, the CO₂ solubility in the hybrid adsorbent markedly increases in comparison to that found in the raw adsorbent as well as in the bulk solvent.^[7] In a related study, Crousse demonstrated the high solubility of CO₂ in hydrofluoroethers and its application to the synthesis of various cyclic carbonates with excellent selectivities and yields under 5 bar of CO₂ at 80 °C.^[8]

Inspired by the idea of CO₂ oversolubility, we investigated the possibility of using the concept of hybrid adsorbent for the coupling of CO₂ and oxiranes to generate organic cyclic carbonates (OCCs), which are of interest as non protic solvents and precursors in polymer and organic synthesis.^[9] The importance of this catalytic transformation has been highlighted recently by Kleij,^[10] North,^[11] and Kerton.^[12] Among the most widely employed catalysts^[13] are binary systems that combine a suitable nucleophile (most often a halide) and a Lewis acid, such as porphyrine, salen and salphen-based derivatives of Al^[14], Mg^[15], Co^[16], Fe^[17], Nb^[18], Zn^[19], alkali metal halides^[20], imidazolium^[21], phosphonium^[22], and ammonium salts.^[23] In recent years, organocatalysts have also shown promise as an important alternative in the field of CO₂ functionalization.^[24] Metal-free catalysts are robust, nontoxic, cheap, and bench-stable organic molecules that do not necessarily require inert reaction conditions.^[25] Although most catalytic systems require high temperature and pressure, catalysts that operate at low temperature and/or ambient pressure have been reported.^[26] North and co-workers demonstrated that cyclic carbonate synthesis through cycloaddition of CO₂ to epoxides catalyzed by bimetallic Al(III)-salen complexes can be performed under ambient pressure and temperature.^[27] Similarly, Kleij employed structurally simple Zn(salphen) catalyst as a very efficient catalyst for the synthesis of cyclic carbonates from CO₂ and terminal epoxides under extremely mild conditions, such as room temperature and 2 bar of CO₂.^[28]

In recent years, solid materials were reported as interesting catalytic alternatives.^[29] In that sense, Werner synthesized bifunctional ammonium salts covalently bound to polystyrene or silica supports, which proved to be efficient and recyclable catalyst for the solvent-free synthesis of cyclic carbonates from

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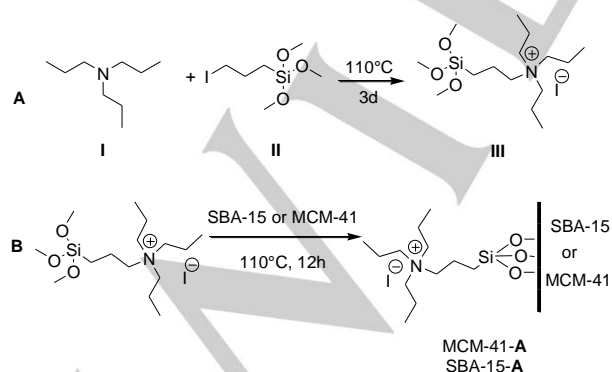
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epoxides at 90 °C and 10 atm of CO₂.^[30] Bai and colleagues synthesized a Co porphyrin complex immobilized on magnetic nanoparticles.^[31] This heterogeneous catalyst showed over 90% conversion of propylene carbonate under 10 bar of CO₂ and could be recycled up to 16 times using a magnet. North and colleagues also reported the synthesis of bimetallic aluminium(salen) complexes supported on silica capable of catalyzing the synthesis of cyclic carbonates from epoxides and carbon dioxide produced by the combustion of natural gas or coal. Interestingly, the loss of catalyst activity observed was attributed with a change of morphology of the catalyst which prevented the epoxide and carbon dioxide to access the active sites rather than leaching of the catalyst, thus demonstrating the importance of catalyst morphology.^[32] We wish to extend on the importance of catalyst morphology on catalytic activity by reporting oversolubility as a powerful tool to promote the ring opening of epoxides in presence of CO₂ to generate cyclic carbonates under unprecedented mild conditions, i.e., the absence of Lewis acid catalyst, at room temperature and 1 bar of CO₂.

Both SBA-15 and MCM-41 materials were prepared according to well-established procedures.^[33] Catalytically active ammonium salt modified with trimethoxysilane anchoring group (**III**) was synthesized by the conversion of readily available tripropylamine **I** with iodopropyltrimethoxysilane **II** for 3 days at 110 °C (Scheme 1, **S1-S4** for ¹H, ¹³C, ²⁹Si, MASS spectra, SI). The grafting of **III** on the surface of the silica materials was carried out at 110 °C in dry toluene under an inert atmosphere. The resulting functionalized solids are referred as SBA-15-**A** and MCM-41-**A**. Furthermore, we have opted to passivate the surface of MCM-41-**A** or SBA-15-**A** materials using TMDS as the silylation agent, generating respectively materials MCM-41-**A**-TMDS and SBA-15-**A**-TMDS.^[34]

Low temperature N₂ physisorption isotherms and pore-size distribution (PSD) profiles of starting and functionalized materials (Figure **S5**, SI) confirm a decrease of the pore size from 4.2 nm for MCM-41 to 3.5 nm for both MCM-41-**A** and MCM-41-**A**-TMDS, and from 8.1 for SBA-15 to 7.3 and 7.0 nm, for SBA-15-**A** and SBA-15-**A**-TMDS, respectively (Table **S1**, SI).

Additionally, a significant decrease of surface area was observed after ammonium salt grafting and surface passivation for both SBA-15 and MCM-41 materials (Table **S1**). Thermogravimetric analysis shows a grafting of approximately 12-13% (w/w) of ammonium salt which generates 0.38 and 0.42 mmol/g of catalytically active nucleophilic centers on the surface of SBA-15-**A** and MCM-41-**A** materials, respectively. XPS results, however, provided a lower value of surface iodide concentration, 0.23 and 0.30 mmol/g for SBA-15-**A** and MCM-41-**A**, respectively. Solid state ¹³C CP/MAS NMR as well as FTIR spectroscopy confirm the preservation of tetrapropylammonium salt after being grafted on the surface of SBA-15-**A** and MCM-41-**A** (Figure **S10** (i) and (ii) for MAS NMR and **S11** for FTIR, ESI). By performing the conversion of styrene oxide to styrene carbonate in excess of acetone under atmospheric pressure of CO₂ using MCM-41-**A** and SBA-15-**A**, two products that do not correspond to the desired cyclic carbonate along with the desired product were observed for both systems. Changing the reaction parameters, such as the molarity of starting compounds as well as the catalyst loading from 5 to 1000 mol % did not seem to have an influence on the final products, although the proportion of each product changed significantly (Table **S2**, SI). NMR characterization of the isolated products allowed to identify iodohydrin species **IV** and **V** (Scheme 2) (for spectra, see Figures **S6-S9**, SI). Both products are characteristic of the ring opening of the oxirane resulting from a nucleophilic attack of the iodide of the materials. Formation of **IV** and **V** could originate from the protonation of the iodo-alkoxide product generated from either residual water or silanol groups. Since there is no chemical activation of the starting epoxide, which dictates the direction of nucleophilic attack, iodide may approach either oxirane carbon atoms (Scheme 2). Even after complete elimination of water from the reaction mixture, undesired iodohydrins **IV** and **V** were still the major side-products since surface silanols (pK_a = 2, 8.2)^[35], are also capable to readily donate protons to more basic iodo-alkoxide (pK_a = 13.2).^[35,b] In contrast, the use of passivated materials, MCM-41-**A**-TMDS and SBA-15-**A**-TMDS, did not generate iodohydrins.



Scheme 1. A. Synthesis of tripropylammonium salt **III**; B. Grafting of ammonium salt onto the surface of mesoporous silica.

Scheme 2. Side reaction occurring during the synthesis of styrene oxide.

For the synthesis of cyclic carbonates using oversolubilized CO₂, the starting epoxide was used as the physical solvent as well as starting reagent. Therefore, we studied hybrid adsorbents based on SBA-15-A-TMDS and MCM-41-A-TMDS solid materials filled with styrene oxide and hexene oxide. For consistency and accurate comparison of material efficiency, all the catalytic tests were performed keeping the epoxide-to-iodide ratio equal to 10 mol%, pressure of CO₂ of 1 and 3 bar and a temperature of 25 °C. First, styrene oxide was reacted with CO₂ in the presence of different solid supports with variation of CO₂ pressure (Table 1) in order to determine the effect of the support. A reaction using neat styrene oxide and tetrapropylammonium iodide provided yields inferior to 13 and 8% with 1 and 3 bar of CO₂, respectively (entry 1). Besides, significant amount of side-product **V** was observed. Such a poor reactivity could easily be explained by a low solubility of the ammonium salt in styrene oxide. When SBA-15-A-TMDS and MCM-41-A-TMDS hybrid systems were used under oversolubility conditions, excellent yields were obtained, even for low pressure of CO₂ (1 atm), providing respectively 86% (entry 2) and 99% (entry 3) of the desired cyclic carbonate. No side-products **IV** or **V** were observed.

Table 1. Yields of styrene carbonate for different solid catalytic systems.

Entry	Material	Styrene carbonate yield [%] ^[a]	
		1 bar	3 bar
1	no solid catalyst	13	8
2	SBA-15-A-TMDS-cycle1	86	89
3	MCM-41-A-TMDS-cycle1	99	95
4	MCM-41-TMDS + TPAI-cycle1	96	N/A ^[b]
5	MCM-41-TMDS + TPAI-cycle2	7	N/A ^[b]
6	SBA-15-TMDS + TPAI-cycle1	93	N/A ^[b]
7	SBA-15-TMDS + TPAI-cycle1	≤5%	N/A ^[b]
8	SBA-15-A-TMDS-cycle2	88	N/A ^[b]
9	SBA-15-A-TMDS-cycle3	20	N/A ^[b]
10	MCM-41-A-TMDS-cycle2	96	N/A ^[b]
11	MCM-41-A-TMDS-cycle3	96	N/A ^[b]
12	MCM-41-A-TMDS-cycle4	92	N/A ^[b]

Reaction conditions: modified silica 0.5 g, styrene oxide 0.22-0.4 g (mass is different for MCM-41-A-TMDS and SBA-15-A-TMDS, I/epoxide=0.1), no additional solvent, p(CO₂)=1 and 3 bar, 24 h, r.t.

[a] Isolated yield. [b] Salt impregnation experiments and multicycle stability were tested for 1 bar of CO₂.

Furthermore, tetrapropyl ammonium iodide (TPAI) salt was impregnated into the pores of MCM-41-TMDS and SBA-15-TMDS solids and the resulting catalytic activity was tested over 2 cycles. Analogously to MCM-41-A-TMDS and SBA-15-A-TMDS, high activity was observed after the first catalytic cycle performed at 1 bar of CO₂ and room temperature, providing 96% (entry 4) and 93% (entry 6) for MCM-41-A-TMDS and SBA-15-A-TMDS silica, respectively. However, since the ammonium salt is not attached covalently inside the pores, a complete loss of catalytic activity was observed for the second cycle and only 7% (entry 5) and ≤5% (entry 7) of styrene carbonate was obtained for MCM-41-TMDS and SBA-15-TMDS, respectively, which is explained by the leaching of the active nucleophile in the system. This proves the importance of the covalent attachment of nucleophile inside the pores. Subsequently, the efficiency of SBA-15-A-TMDS and MCM-41-A-TMDS systems were compared over three catalytic cycles of styrene oxide conversion in order to identify which system exhibits higher reactivity through a possibly more pronounced oversolubility effect at atmospheric pressure of CO₂. MCM-41-A-TMDS system exhibited better reactivity over 4 cycles with preservation of high styrene carbonate yield (entries 8-12), while the efficiency of SBA-15-A-TMDS decreased significantly after 3 cycles, providing only 20% of final product (entries 8 and 9). Such reactivity drop is accompanied by the loss of the grafted ammonium catalyst content, which decreases by 10 wt% after 3 cycles (Table S3, SI). Besides, surface area of the recovered SBA-15-A-TMDS-cycle3 material increased from 467 to 535 m²/g, which could be also explained by elimination of iodide as well as grafted ammonium species from the surface of the support after multiple centrifuging cycles, making MCM-41-A-TMDS a better hybrid adsorbent for cyclic carbonate synthesis. No significant loss of catalytic activity was detected also after 4 cycles since yield and selectivity for styrene carbonate constantly remained above 90% (entry 12). Higher efficiency of the MCM-41-based hybrid adsorbent is in line with previous studies where MCM-41-based mesoporous materials exhibited higher adsorption capacity of CO₂.^[6] Hexene oxide was additionally tested as a substrate for the synthesis of 4-butyl-1,3-dioxolan-2-one (Table 2). Both systems showed good activity and provided 86% (entry 1) and 70% (entry 2) for SBA-15-A-TMDS and MCM-41-A-TMDS, respectively. However, in the case of SBA-15-A-TMDS, the increase of CO₂ pressure from 1 to 3 bar did not permit to obtain better reactivity, oppositely, the yield of the corresponding carbonate decreased from 86% to 26% (entry 1). The reason of such behavior is still unclear, but it was not observed for MCM-41-A-TMDS catalyst, which provides slightly better reaction yield after the pressure was augmented.

Table 2. Results of catalytic cycloaddition of carbon dioxide to styrene oxide and hexene oxide.

Entry	Material	Styrene carbonate yield [%] ^[a]		4-butyl-1,3-dioxolan-2-one yield [%] ^[a]	
		1 bar	3 bar	1 bar	3 bar
		1	SBA-15-A-TMDS	86	89
2	MCM-41-A-TMDS	99	92	70	73

Reaction conditions: modified silica 0.5 g, styrene oxide 0.22-0.4 g (mass is different for MCM-41-A-TMDS and SBA-15-A-TMDS, I⁻/epoxide=0.1), neat, p(CO₂)=1 and 3 bar, 24 h, r.t.

[a] Isolated yield.

In conclusion, we have demonstrated that the physical phenomenon of gas oversolubility in nanoconfined liquids, i.e., nanoliquids, could be successfully applied for chemical transformations. The hybrid adsorbents were prepared by confining a physical solvent (epoxides) into the pores of MCM-41 and SBA-15 solid supports, where the presence of solvent molecules favors the layering of CO₂ molecules within the pores. Therefore, the CO₂ solubility in the hybrid adsorbent markedly increases in comparison to that found in the raw adsorbent as well as in the bulk solvent, without “chemical” activation of CO₂. Particularly, it was very useful for the efficient and greener cycloaddition of carbon dioxide to epoxides, such as styrene and hexene oxides. No organometallic catalyst was needed and only efficient nucleophile deposition on the surface of a solid support is required, which yielded effective, durable catalytic system. Since both MCM-41-A-TMDS and SBA-15-A-TMDS systems are capable to efficiently operate at atmospheric pressure of CO₂ and room temperature, it is now possible to apply the obtained hybrid sorbents/catalysts in flow process, which could potentially be scaled-up. A flow chemistry three-phase reaction for cyclic carbonate production and expanding of the scope of possible catalytic transformations requiring pressurized CO₂ can thus be envisioned.

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Carbon Dioxide Oversolubility in Nanoconfined Liquids for the Synthesis of Cyclic Carbonates

The physical phenomenon of gas oversolubility in nanoconfined liquids was applied for the catalytic cycloaddition of carbon dioxide to epoxides to generate cyclic carbonates at room temperature under atmospheric pressure. A hybrid adsorbent based on MCM-41 silica material exhibits enhanced catalytic properties and multi-cycle stability, providing an effective and sustainable catalytic system.