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Thermoresponsive Hydrogels in Catalysis

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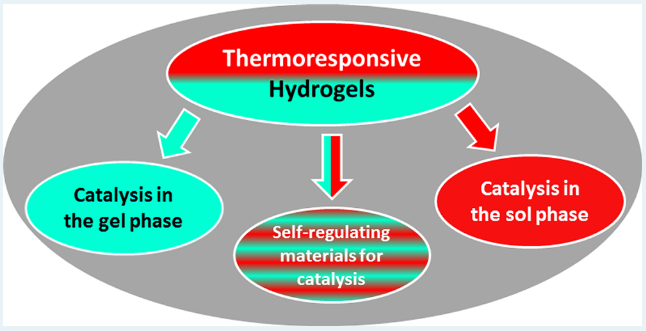
ABSTRACT: The tunable properties of thermoresponsive physical hydrogels recently found application in catalysis. The most relevant examples are described in this perspective article. Novel concepts are especially highlighted through the beneficial effects of thermoresponsive hydrogels on the catalytic performance. Their scope and future developments are also addressed.



KEYWORDS: *hydrogel, catalysis, thermoresponsive systems, soft matter, polymers*

INTRODUCTION

The increasing interest in hydrogels during the past ten years reveals their ability to significantly modify our perception of matter. Hydrogels have become one of the most extensively studied soft materials and currently continue to fascinate researchers throughout the world. Their flexible three-dimensional networks have unique properties and could be considered as solid-like materials with the fluidity of a liquid at a microscale level. This in-between feature allowed for the developments of new applications that could have not been feasible with other materials. Indeed, the use of hydrogels has allowed to overcome problems usually encountered in the solid state or in the liquid phase and has also led to new materials with specific properties. The progress that has recently been made in the field has prompted many researchers to conceive novel systems applicable in so many fields that we will not even attempt to number them. Because of the infatuation for hydrogels, it is legitimate to wonder how important their development could be in the future and what could be their place in our society. Alongside their well-known utilization in medicine, biology, and design of new materials, the question arises whether hydrogels could be used in catalytic applications. Such considerations are relevant because of concerns in sustainability. Catalysis has acquired a pivotal role in processes consisting in transforming reactants into products by environmentally friendly means. In this context, catalysis in aqueous medium is especially attractive as water is the most eco-friendly solvent. As hydrogels contain a huge amount of water, as their name states, they could potentially host within their structure very different kinds of hydrophilic catalysts and/or substrates, thus facilitating contacts between reactive species. Incorporation of catalysts within a hydrogel is not as obvious as it first seems to be. An accurate knowledge of their texture is required so as to optimize the catalyst-distribution throughout the material. Two categories of hydrogels should be distinguished. Conventional hydrogels are three-dimensional networks formed by cross-linked polymers (Figure 1) which are able to swell in the presence of water and shrink in the absence of water. The water holding capacity of hydrogels mainly results from the presence of hydrophilic groups (amino, carboxyl, and hydroxyl groups) in the polymer chains. In chemical (permanent) hydrogels, polymer chains are connected by covalent bonds. Since the bonding between polymer chains is irreversible, no change in the equilibrium swelling is observed upon stimulus application. Permanent hydrogels have already been the subject of many studies in the field of catalysis. For example, Sahiner et al. showed that metallic nanoparticles could be generated in situ inside chemical hydrogels[1,2] and used as a catalyst in metal-catalyzed reduction of nitrophenols[3−6] or hydrogen production by hydrolysis of sodium boron hydride in a basic medium.[7−9] Similarly, gold nanoparticle could be embedded into hydrogel matrixes and used as catalysts in the reduction of 4-nitroaniline.[10] The advantages of such materials

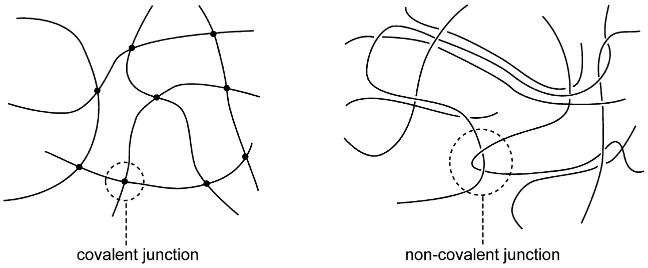


Figure 1. Chemical hydrogel (left) and physical hydrogel (right).

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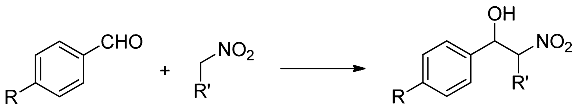
lie in the preparation of well-defined nanoparticles and their stabilization in aqueous media. Moreover, the solid-like properties of chemical hydrogels allow for easy recovery of the gelator by simple filtration once the catalytic reaction is complete. However, diffusion of solutions within the porous network of gels is somewhat slower than in homogeneous systems. Thus, in terms of catalytic performance, no real benefit could be drawn from the 3D-hydrogel network.

In contrast, the constitutive components of physical gels are connected through noncovalent bonds (Figure 1), such as van der Waals forces, metal−ligand coordination, hydrogen bonding, ionic interactions, hydrophobic interactions, or micro- and nanocrystallite formation.[11−16] Two categories of physical hydrogels can be distinguished: polymer and molecular (supramolecular) hydrogels. Polymer physical gels are formed by the growth of physically connected polymer chains.[17,18] Molecular gels, for their part, are formed from low-molecular-weight organic compounds (molecular weight less than 1000 g·mol^{-1}) interacting by noncovalent bonds. The recent development of both polymer and molecular hydrogels has opened new opportunities in the field of soft materials.[19−28] Indeed, as physical gels are held together by multiple weak and therefore reversible interactions, they can be considered as responsive[29] and tunable materials upon changes of environmental factors such as physical stimuli (temperature, pH, light and shear force)[30] or chemical stimuli (acid−base, ions, redox).[31] Upon exposure to external stimuli, the texture of the so-called "smart" hydrogels can be dramatically modified (shape, dimensional change, flexibility, etc.). In fact, stimuli are translated into polymer reconfigurations.[32−35] When removing the external stress, these materials relax back to the original state.[36] Numerous studies have shown how the physicochemical properties of a given physical hydrogel-based system could be dramatically affected by a modification of the hydrogel texture upon exposure to an external stimulus.[37−41] Interestingly, since the bonding between hydrogel components is reversible, physical gels possess sol−gel reversibility. For example, temperature variations can trigger the on−off switching of gelation. Accordingly, their thermoreversibility and temperature sensitivity make physical hydrogels very appealing for catalytic applications as their activity may be conveniently tuned by adjusting the temperature. From these considerations, catalytic systems have been developed aiming at improving the stability, performance, and reusability of a catalyst. Recently, we and others demonstrated that temperature-responsive hydrogels are tunable materials for the catalytic transformation of various organic substrates. Upon temperature variation, the hydrogel properties dramatically changed so that a catalytic process became favorable. This is the purpose of the present perspective article, namely, to highlight recent advances made in the field of thermoresponsive hydrogel-based catalytic systems. Below are detailed some of the main results recently obtained in the field. We will also try to define the contours of what could be the future of thermoresponsive hydrogels in catalysis.

Active Thermoresponsive Hydrogels in the Gel Phase. A base-catalyzed transformation in which the gel phase was participating as the active phase has been implemented by Escuder et al.[42] In that case, the gelator contains terminal L-proline moieties attached to a L-valine-based gelator scaffold. Gel formation in acetonitrile could be explained by the formation of aggregates through multiple H-bonding. The Henry nitroaldol reaction was chosen as a model reaction in which a basic catalyst deprotonated a nitroalkane that afterward attacked the carbonyl of an aldehyde (Scheme 1). Basic catalytic gels gave excellent yields of the nitroaldol product after addition of aromatic aldehydes. Interestingly, the system showed a switchable catalytic performance controlled by temperature. Actually, cooling the system below T_{gel} yielded an active basic system, while the catalytic activity was switched-off above T_{gel} because of disassembly of the hydrogel components into inactive free molecules.

Scheme 1. Henry Nitroaldol Reaction



Another interesting property of physical thermoresponsive hydrogels lies in their ability to deswell/swell reversibly to concentrate substrates and catalysts within the hydrogel matrix and therefore accelerate the reaction rate. To this end, a porous, thermo- and pH-responsive chelating hydrogel of poly(*N*-isopropylacrylamide)-co-poly[2-methacrylic acid 3-(bis-carboxymethylamino)-2-hydroxypropyl ester] (PNIPAAm-co-PMACHE) has been used as both a reaction medium and a metallic-catalyst support (Figure 2).[43] The thermoresponsive segment of PNIPAAm exhibited a hydrophilic/hydrophobic transition in aqueous medium. More precisely, PNIPAAm underwent a large volume change at the volume-phase-transition temperature of ∼32 °C above which the hydrogel deswelled. Water was expelled from the hydrogel matrix (unfavorable entropy of mixing) resulting in higher catalyst and reactant concentrations. The concentration effect proved to be effective in Suzuki and Heck reactions as the studied hydrogel/Pd(0) system was about 14 times of a reference microgel-Pd catalyst.

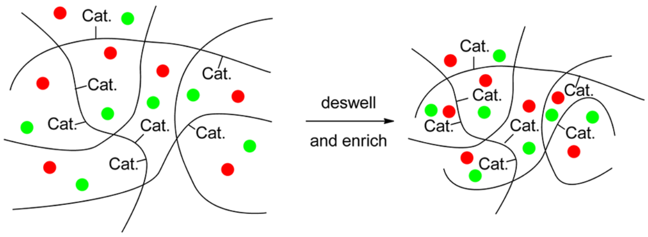


Figure 2. Polymer hydrogel as both reaction medium and metallic-catalyst support.

The same concept has been applied to the preparation of size-controlled Au nanoparticles (Au-NPs) within the PNIPAAm-co-PMACHE hydrogel.[44] Above 27 °C, the thermoresponsive hydrogel can reversibly deswell/swell without affecting the encapsulated AuNPs. Indeed, the average size of the encapsulated Au nanoparticles in the recovered composite was similar to that in the fresh one. Used as catalyst in aerobic alcohol oxidation, the catalytic efficiency of the thermoresponsive composite proved to be a consequence of the increase in alcohol concentration within the hydrogel matrix through the reversible deswelling. One of the main advantages of this technique also lies in the convenient reuse of the hydrogel/Au composite.

Active Thermoresponsive Hydrogels in the Sol Phase. Our group recently elaborated a thermoregulated catalytic

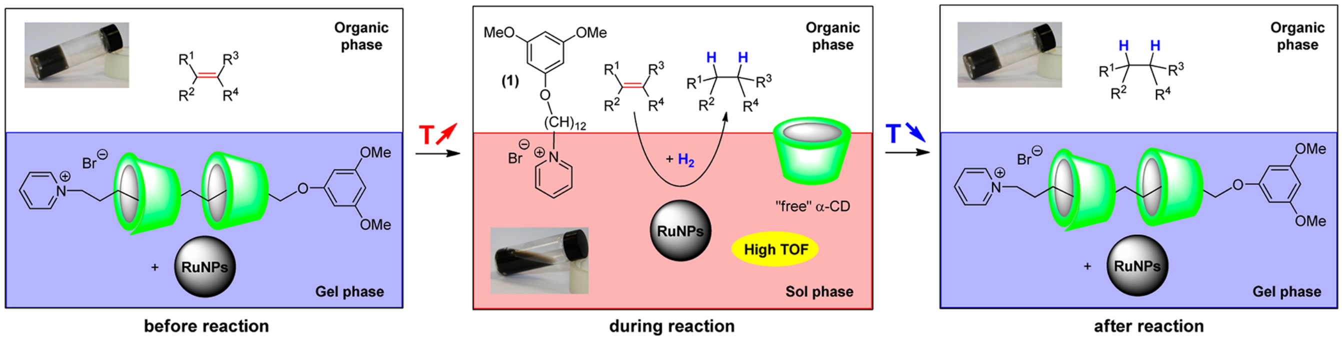


Figure 3. Thermoregulated catalytic system using a metallic RuNPs-containing supramolecular hydrogel matrix.

process using a ruthenium-nanoparticle (RuNPs) catalyst embedded into a supramolecular cyclodextrin(CD)-based hydrogel matrix. Native CDs, a series of cyclic oligosaccharides consisting of α-1,4-linked glucopyranose units, do not undergo gelation in water while host−guest complexes and polyrotaxanes of CDs form hydrogels especially with PEG[45] or smaller molecules such as pyridine[46] of polyaromatic hydrocarbons.[47] In our case, the supramolecular gel was prepared from a mixture of the *N*-alkylpyridinium amphiphile $[\text{py-N-(CH}_2)_{12}\text{OC}_6\text{H}_3\text{-3,5-(OMe)}_2]^+$ (Br^-) (**1**, Figure 3) and α-CDs.[48,49] Such supramolecular hydrogels proved especially effective as templates for in situ RuNPs syntheses. Indeed, we took advantage of the hydrogel template properties to access size-controlled spherical RuNPs in a Gaussian distribution with an average diameter of approximately 1.6 nm and a homogeneous dispersion without any aggregates.[50] RuNPs@**1**•(α-CD)$_2$ nanocomposite hydrogels were obtained once RuNPs were embedded in the polymer matrix. Moreover, the hydrogel thermo-reversibility allows for the stabilization of NPs at room temperature and their activation at high temperature. More precisely, once metallic NPs have been embedded into a supramolecular hydrogel matrix, the system was heated above the sol−gel transition temperature (39 °C). The hydrogel became a free-flowing solution when heated above 39 °C and returned to a gel state when cooled at room temperature. Thus, upon accurate control of the temperature, the self-assembled hydrogel texture could be switched from gel to sol at will. The catalytic performance of the RuNPs@**1**•(α-CD)$_2$ thermoresponsive hydrogel has been evaluated in hydrogenation of hydrophobic and hydrophilic alkenyl substrates. The Ru-catalyzed reaction took place in the sol phase at 50 °C with turnover frequency up to 350 h^{-1} (Figure 3). Upon cooling, the catalyst-containing hydrogel and the products could be separately recovered in two distinct phases. Additionally, once the reaction was complete, RuNPs did not aggregate but remained homogeneously dispersed in the three-dimensional hydrogel matrix allowing for their reusability. The robustness and stability of the catalyst were thus greatly improved. The catalysis results were rationalized on the basis of two distinct and yet complementary aspects: (i) the enhanced probability of contact between components in the sol phase and (ii) the presence of high "free CD and **1**" proportions because of the partial dissociation of a self-assembled [3]pseudorotaxane **1**•(α-CD)$_2$ at high temperature.[51] The reusability of the catalytic system has been successfully examined without any loss of its catalytic activity.

Self-Regulating Thermoresponsive Hydrogels. Aizenberg et al. very recently reported a hydrogel-based system capable of continuous self-monitoring and self-regulating behavior. They combined two nano/microstructured surfaces and hydrogels to create a bioinspired class of hybrid materials in which two integrated but structurally distinct elements interacted. The surface was constituted of arrays of nanostructures whose generally static functions could be reversibly reconfigured in response to stimuli by embedding them in a layer of temperature-responsive hydrogel. More precisely, a catalyst was physically adsorbed or chemically attached to the tips of the microstructures and the resulting self-assembled system was immersed within the temperature-responsive hydrogel. The hydrogel-supported, catalyst-bearing nano/microstructure was then covered with a reactant-containing layer, leading to a self-regulated mechanical-chemical adaptively reconfigurable tunable system (SMARTS) that could undergo on/off mechanical actuation of microstructures through reversible external or internal chemical stimuli. For example, upon exposure to temperature variations, the response of the swelling/contracting gel induced the catalyst to move into and out the reactant layer, thus acting as an on/off switch for chemical reactions (Figure 4). In fact, the hydrogel acted as a muscle that moved the catalyst into and out of a top layer of reactants. The reaction was turned on when the catalyst-bearing microstructures straightened (swollen hydrogel) and turned off when they bent (contracted hydrogel). The chemical output signal was matched with the stimulus of the responsive hydrogel. These homeostatic materials closely resemble living organisms in the sense that they could control their local environment through interconversions of chemical and mechanical energy and self-regulating feedback loops.

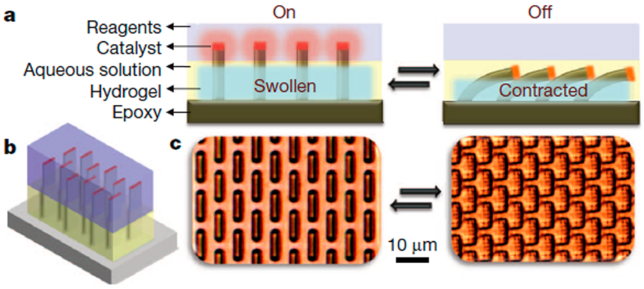
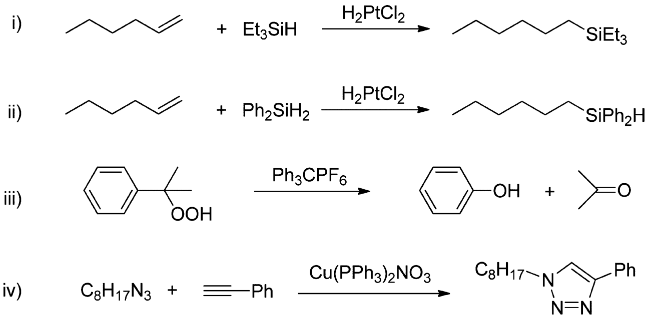


Figure 4. (a) Cross-section schematic. (b) Three-dimensional schematic. (c) Top-view microscope images of upright and bent microfins corresponding to on (left) and off (right) reaction states. (Reprinted with permission from *Nature* **2012**, *487*, 214. Copyright 2012 Nature Publishing Group).

The proof-of-concept of SMARTS has been applied to organic, inorganic, and biochemical reactions using poly(*N*-isopropylacrylamide) (poly(NIPAAm)) as a temperature-responsive gel which shows negative temperature responsive behavior.[52−54] The homeostatic temperature of the catalytic system could be controlled by the lower critical solution temperature (LCST) of the responsive gel. Below the LCST, the polymer was in its swollen state. Above the LCST, the water molecules are expelled, and the hydrogel collapsed to its deswollen state. Four exothermic catalytic reactions have been considered (Scheme 2): (i) hydrosilylation of 1-hexene with triethylsilane catalyzed by H_2PtCl_6 (Et, ethyl), (ii) hydrosilylation of 1-hexene with diphenylsilane catalyzed by H_2PtCl_6 (Ph, phenyl), (iii) decomposition of cumene hydroperoxide catalyzed by Ph_3CPF_6, (iv) "click" reaction between octylazide and phenylacetylene catalyzed by $Cu(PPh_3)_2NO_3$.

Scheme 2. Exothermic Reactions As Proof-of-Concept of SMARTS



Below the LCST of poly(NIPAAm) (32 °C), the embedded microstructures straightened as the thermally responsive hydrogel swelled so that the catalyst-functionalized tips could be found intruding into the reagent layer. An exothermic reaction could then take place between the reagents and the catalyst. As the reaction temperature increased, a contraction of the hydrogel occurred above the LCST, and the catalyst-bearing microstructures were removed from the reagent layer until the temperature came down to the LCST. Accordingly, continuous, self-regulated oscillations could be generated playing on the LCST of the hydrogel. By adjusting the reagent concentration (control of rate of heat generation), the height of the liquid interface, or the microstructure dimension/geometry, the autonomous temperature oscillations could be finely tuned.

■ OUTLOOK

Throughout the above studies, we intended to highlight the range of possibilities that thermoresponsive hydrogels offer in the field of catalysis. It appears that they are very interesting media for catalytic applications. Their unique properties allowed for the development of very different catalytic systems benefiting from the ability of the hydrogel network to modify its 3D-structure upon heating or cooling. From a practical point of view, several advantages could be gained from the utilization of thermoresponsive hydrogels in catalysis. Catalytic events could be controlled through reversibility of the hydrogel network structure. For example, deswelling the hydrogel matrix led to increased concentrations in reactants and catalysts. Upon heating, hydrogels could also be used in the sol phase to favor contacts between reactants and metal-nanoparticle catalysts. Once the reaction was complete, the catalytic system was cooled and the catalyst could be easily recovered by simple decantation. We anticipate that, in the future, the sol−gel transition could also be used with monometallic species, thus expanding the scope of these stimuli-responsive materials. An oscillating activation/deactivation process involving catalyst-bearing microstructures could also be controlled by repetitive swelling/deswelling cycles. As such, as reported by Aizenberg et al., "SMARTS could be used in autonomous self-sustained thermostats with applications ranging from medical implants that help stabilize bodily functions to 'smart' buildings that regulate thermal flow for increased energy efficiency". However, though thermoresponsive hydrogels possess numerous advantages, their application in catalysis could be hampered by several drawbacks. First, the hydrogel viscosity should be carefully determined to avoid diffusion limitations of reactants and catalysts. A huge drop in catalytic activities could result from the hydrogel in the sol phase being too viscous. Additionally, once formed, products could accumulate within the hydrogel, thus altering the hydrogel texture and its ability to reform into a gel phase. This is of importance especially for hydrogel-based catalytic processes for which the hydrogel phase is recycled.

In Table 1 are gathered the pros and cons of catalytic systems based on thermoresponsive hydrogels. A comparison between thermoresponsive hydrogels and other catalytic systems highlighted the specificity of these materials especially in terms of adaptability and self-regulating ability. As such, thermoresponsive hydrogels constitute a special class of media for catalysis.

To sum up, the utilization of themoresponsive hydrogels in catalysis is highly feasible provided that the hydrogel structure has been carefully designed. A broad choice of chemical reactions could be exploited owing to tunable properties of the hydrogel texture. Thermoresponsive hydrogels could especially be used as actuator because of their ability to change their texture upon temperature variations. On/off switch-type

Table 1. Comparison between Reusable Catalytic Systems

catalytic system	pros	cons
supercritical CO_2	friendly solvent, product recovery by simple depressurization, safety, heat transfer and thermodynamic attributes, readily available, cheap, nontoxic, and nonflammable	'weak' solvent (low polarity, dielectric, dipole moment), not suitable for high-molecular-weight compounds (proteins, polymers, etc.)
ionic liquids	no measurable vapor pressure, good solvents for many organic and inorganic compounds, stabilizes sensitive compounds, thermally and hydrolytically stable	aquatic toxicity, viscosity, combustible, poor biodegradability, expensive in comparison with molecular solvents, freezes at relatively high temperature, synthesis of appropriate ligands
aqueous catalysis	cheap, nontoxic, readily available, extremely high specific heat capacity	require water-soluble ligands to immobilize the catalyst in aqueous phase, not suitable for hydrophobic substrate (>C6), recovery of the end-of-life catalyst
catalyst immobilization on solid support	increased catalyst lifetime and catalytic efficiency, implementation in continuous flow	ligand synthesis, metal leaching, stability of the support, catalytic fouling
thermoresponsive hydrogels	adaptability, compatible with heterogeneous catalysts, oscillating activation/deactivation process	synthesis of appropriate ligands, viscosity, possible accumulation of products within the hydrogel matrix (destructuring)

catalytic systems could be conceivable with applications in organo-, metallic-, and organometallic-catalyzed reactions. The doors opened by the pioneering works cited above would probably stimulate more innovative applications in catalysis.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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