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Nanoparticle-Based Catalysis using Supramolecular Hydrogels

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Abstract: A thermoregulated catalytic process has been elaborated using a ruthenium-nanoparticle catalyst embedded into a supramolecular cyclodextrin-based hydrogel matrix. Upon heating, the gel phase turned into a sol phase in which alkenes could be efficiently hydrogenated. Upon cooling, the reaction products and the metallic catalyst could be easily separated. The reusability of the system was clearly demonstrated.

Keywords: cooperative effects; cyclodextrins; host-guest systems; inclusion compounds; supramolecular chemistry

Hydrogel applications have become very popular in recent years, especially in biology and medicine.[1] However they currently have an impact on other areas such as materials[2] or catalysis.[3] For instance, polymer hydrogels proved especially effective as templates for *in situ* metal nanoparticles (NPs) syntheses. Once the NPs are embedded in the polymer matrix, the nanocomposite hydrogels could even be used as a reactor in the metal-catalyzed reduction of nitrophenols[4] or hydrogen production.[5] Parallel to classic hydrogelators, supramolecular gels have gained increasing interest, particularly in the development of stimuli-responsive materials.[6] One of the main advantages of supramolecular over polymer hydrogels lies in the non-covalent intermolecular interactions between the hydrogel components that allows for thermal reversibility. Generally speaking, the hydrogel becomes an isotropic solution when heated and returns to a gel state when cooled at room temperature.[7] However, hydrogels have also been described that turn into a clear solution upon cooling to room temperature and are re-formed when heated to the gelling temperature.[8] Thus, by controlling the temperature, the self-assembled hydrogel texture can be switched from gel to sol at will. Astonishingly, the thermoresponsive character of hydrogels has never been taken into account in catalysis.

In this study, we took advantage of the hydrogel template properties to access size-controlled metallic nanoparticles (NPs). Moreover, the hydrogel thermoreversibility 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. A metal-catalyzed reaction could then take place in the sol phase (Figure 1). Upon cooling, the catalyst-containing hydrogel and the products could be separately recovered in two distinct

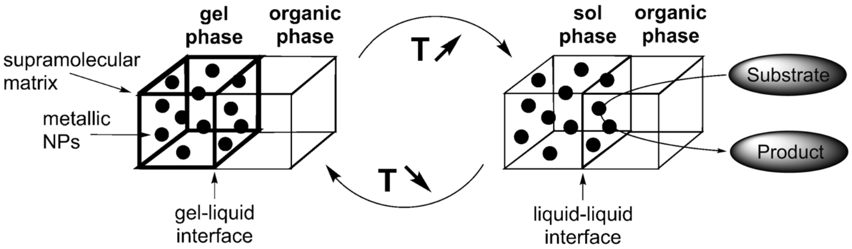
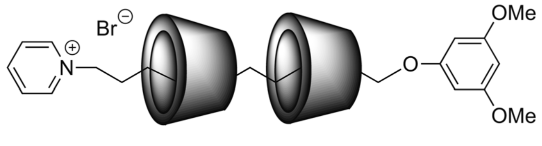


Figure 1. Thermoregulated catalytic system using a metallic NPs-containing supramolecular hydrogel matrix.



$1 \cdot (\alpha\text{-CD})_2$

Scheme 1. Thermoresponsive $1 \cdot (\alpha\text{-CD})_2$ hydrogel obtained by self-assembling of **1** and two α-CDs.

phases. Additionally, once the reaction was complete, NPs did not aggregate but remained homogeneously dispersed in the 3-D hydrogel matrix allowing for their reusability. The robustness and stability of the catalyst were thus greatly improved.

Herein, the concept has been validated in an RuNPs-catalyzed hydrogenation of alkenes. The supramolecular gel was prepared from a mixture of the *N*-alkylpyridinium amphiphile [py-*N*-$(CH_2)_{12}OC_6H_3$-3,5-$(OMe)_2]^+$ (Br^-) (**1**) and α-cyclodextrins (α-CD).[9]

Once mixed in water, **1** and α-CD resulted in a self-assembled [3]pseudorotaxane $\mathbf{1} \cdot (\alpha\text{-CD})_2$ (Scheme 1), characterized by a sol-gel transition temperature of 42 °C.[9] In fact, the amphiphilic character of **1** was masked by inclusion of the alkyl chain into the CD cavities resulting in the formation of a hydrogel. The choice of **1** as a hydrogel component has been guided by two properties. First, pyridinium and dimethoxyphenyl groups have been reported to stabilize RuNPs in aqueous media.[10] Second, we anticipated that, at high temperature, the association constant between the α-CDs and **1** would be sufficiently lowered to dissociate, at least partially, the two α-CDs and **1**. The resulting mixture of "free" CDs and **1** was expected to have a significant impact on the mass transfer between the aqueous NPs-containing phase and the substrate-containing organic phase. Indeed, free α-CD and **1** could act as supramolecular carrier and as surfactant, respectively.

Incorporation of $RuCl_3$ within the hydrogel network followed by a subsequent reduction of the Ru salt in the presence of $NaBH_4$ led to gel-embedded RuNPs, namely RuNPs@$\mathbf{1} \cdot (\alpha\text{-CD})_2$. The morphology and size of the resulting colloidal nanocomposite hydrogel particles were determined by transmission electron microscopy (TEM). The TEM micrographs revealed spherical RuNPs in a Gaussian distribution with an average diameter of approximately 1.6 nm and a homogeneous dispersion without any aggregates (Figure 2).

The particles size is smaller than that observed using surfactants[11] or ionic liquids[12] as RuNPs stabilizing agents, thus highlighting the effective control exerted by the hydrogel internal network structure over the RuNPs growth. The RuNPs being in a constrained environment, their size and shape are likely modulated by the volume of the hydrogel nano-regions.

Viscosity measurements of the nanocomposite material yielded a sol-gel transition temperature of 39 °C (Figure 3) below which the gel predominated and above which a liquid phase was obtained (Figure 4). Moreover, RuNPs@$\mathbf{1} \cdot (\alpha\text{-CD})_2$ is considered thixotropic as the viscosity curve profiles show (i) almost complete reversibility when varying the shear rate and (ii) a time-dependent decrease in the viscosity induced by flow.[13]

The catalytic performances of the RuNPs@$\mathbf{1} \cdot (\alpha\text{-CD})_2$ thermoresponsive hydrogel have been evaluated in hydrogenation of hydrophobic and hydrophilic alkenyl substrates (Table 1). When the reaction pro-

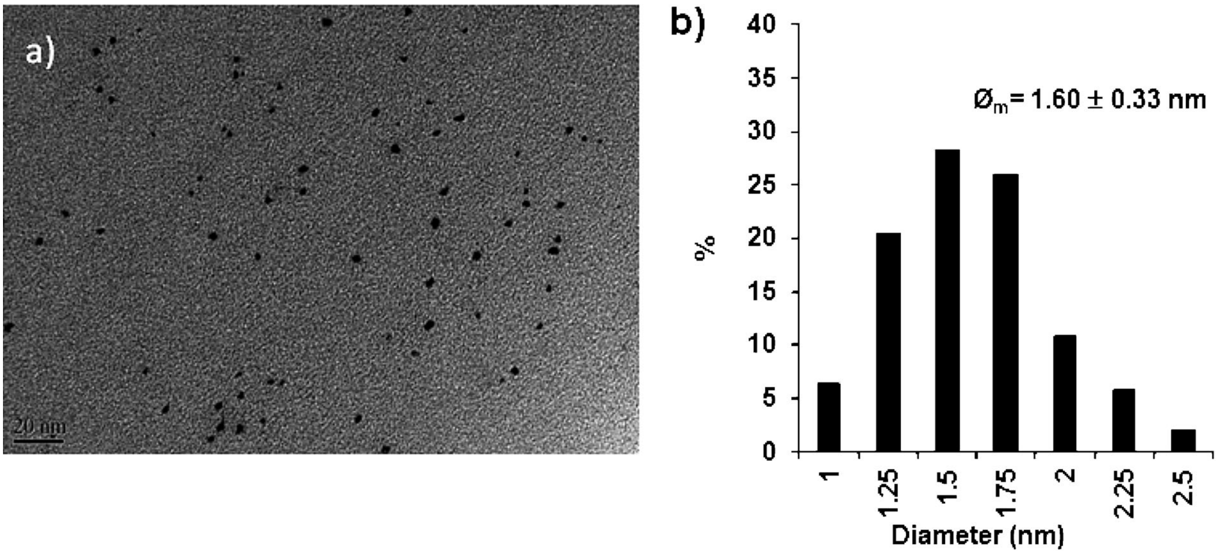


Figure 2. a) Transmission electron micrograph and **b**) size distribution of RuNPs@$\mathbf{1} \cdot (\alpha\text{-CD})_2$.

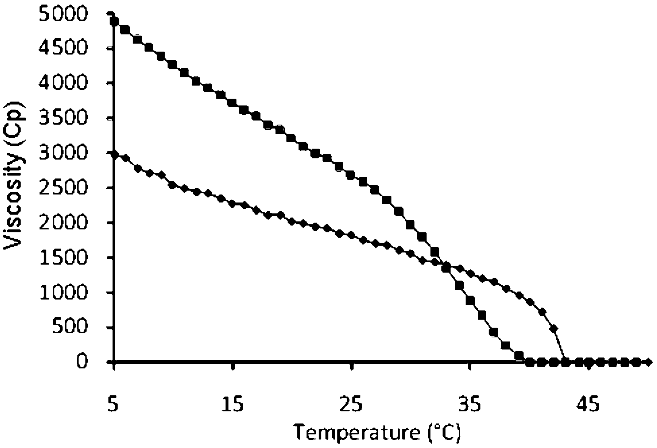


Figure 3. Viscosity curves as a function of temperature of **1**·(α-CD)$_2$ (◆) and RuNPs@**1**·(α-CD)$_2$ (■).

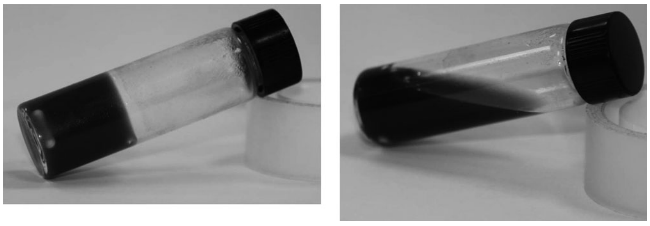


Figure 4. Photographs of RuNPs@**1**·(α-CD)$_2$ at room temperature (*left*) and 50 °C (*right*).

Table 1. RuNPs-catalyzed hydrogenation of terminal alkenes.[a]

Entry	Substrate	H_2 [bar]	Temp. [°C]	TOF [h^{-1}][b]
1	2-methyl-3-buten-2-ol	10	20	28
2	1-decene	10	20	4
3	1-undecene	10	20	5
4	1-hexadecene	10	20	6
5	1-decene	10	50	133
6	1-decene	40	50	300
7[c]	1-decene	40	50	300
8[d]	1-decene	40	50	300
9	1-undecene	10	50	80
10	1-undecene	40	50	240
11	1-hexadecene	10	50	50
12	1-hexadecene	40	50	200
13	2-methyl-3-buten-2-ol	10	50	100
14	2-methyl-3-buten-2-ol	40	50	350

[a] *Conditions:* 1.9×10^{-5} mol catalyst; 5 mL water; stirring at 750 rpm; substrate/Ru = 100.
[b] Determined by GC analysis after total conversion of the substrate. TOF = turnover frequency defined as number of mol of converted substrate per mol of total ruthenium per hour.
[c] Second run using the recovered hydrogel of entry 6.
[d] Third run using the recovered hydrogel of entry 7.

ceeded in the gel phase at room temperature, very low catalytic activities were measured. In these conditions, the better result was logically obtained in hydrogenation of a water-soluble substrate, namely 2-methyl-3-buten-2-ol (Table 1, entry 1, TOF = 28 h^{-1}). Conversely, when the reaction proceeded at 50 °C in the sol phase under stirring, high turnover frequencies (TOF) were obtained whatever the nature of the substrate. Note that no isomerization of the C=C double bonds could be observed during the reaction.

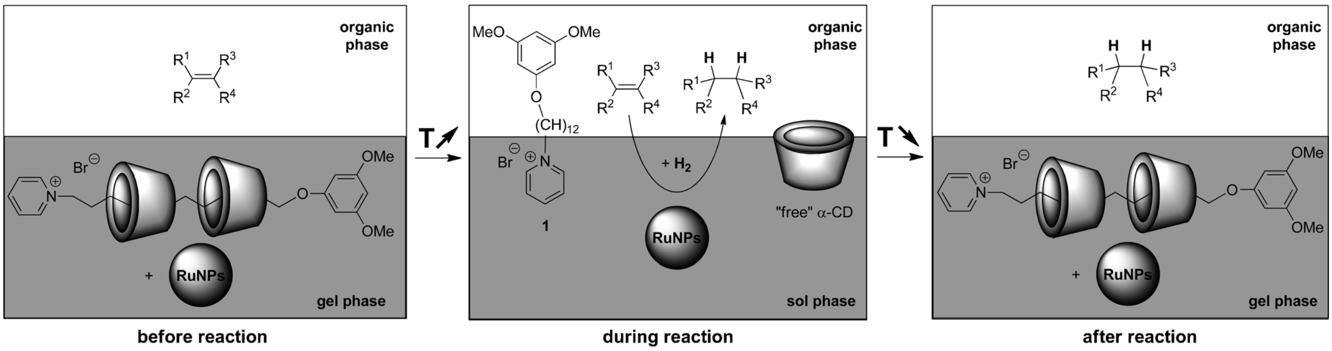
The catalysis results were rationalized on the basis of two distinct and yet complementary aspects: (i) the enhanced probability of contact between components in the sol phase and (ii) the presence of high "free CD and **1**" proportions due to the partial dissociation of a self-assembled [3]pseudorotaxane **1**·(α-CD)$_2$ at high temperature.[14] At 50 °C, an alkyl chain length-dependence was observed whatever the H_2 pressure (Table 1, compare entries 5, 9 and 11 or entries 6, 10 and 12). Actually, the shorter the substrate alkyl chain, the higher is the TOF. This logically results from the more marked hydrophobicity of long alkyl chains towards the hydrophilic hydrogel and highlights the interfacial nature of the catalytic process. Once the reaction was complete, the mixture was cooled at room temperature to recover RuNPs@**1**·(α-CD)$_2$ and the hydrogenated product into two distinct phases (Scheme 2). The reusability of the catalytic system has been successfully examined without any loss of its catalytic activity. For example, with 1-decene as substrate, the TOF remained constant (entries 6–8) after three consecutive substrate reloadings and sol-gel transitions. TEM of aliquots of the recovered hydrogels after each reaction confirmed the RuNPs stability when embedded into the hydrogel network in these catalytic conditions. Indeed, no variation in the RuNPs size could be observed (see the Supporting Information).

To sum up, these results demonstrate that a supramolecular cyclodextrin-based hydrogel matrix allows the stabilization at room temperature and the activation at high temperature of RuNPs catalysts. Futhermore, the RuNPs catalyst stabilized inside the hydrogel matrix can be easily recovered and recycled by a simple phase separation. Extension of the concept to other catalytic reactions is currently on-going.

Experimental Section

Colloidal Suspension Elaboration

Ruthenium chloride hydrate $RuCl_3 \cdot xH_2O$ (5 mg, 0.02 mmol) was dissolved in 5 mL deionized water. α-CD (487 mg,



Scheme 2. Thermoregulated RuNPs-catalyzed hydrogenation of alkenes using the **1**·(α-CD)$_2$ hydrogel matrix. During the reaction, the "free CD and **1**" molecules contribute to the mass transfer between the aqueous phase and the organic phase.

0.5 mmol, 25 equiv.) was added to the solution and **1** (120 mg, 0.25 mmol, 12.5 equiv.) was then poured onto the obtained mixture. The solution was heated at 50 °C and $NaBH_4$ (6 mg, 0.15 mmol, 7.5 equiv.) was quickly added. The reduction was characterized by a color change from brown to black. After addition of $NaBH_4$, the colloidal suspension was immediately cooled to 10 °C. The obtained colloidal suspension in the gel state was kept at low temperature without any nanoparticles aggregation even after several months' storage.

General Procedure for Hydrogenation

A stainless steel autoclave was heated at 50 °C and charged with 5 mL standard Ru(0) colloidal suspension. After a colloidal suspension in the "sol" state was obtained, the substrate (3.8 mmol, 100 equiv.) was poured into the autoclave and hydrogen was admitted to the system up to the desired pressure [$10 < P(H_2) < 40$ bar]. The mixture was magnetically stirred (750 rpm) at 50 °C. The reaction was monitored by analyzing aliquots of the reaction mixture with a Shimadzu GC-17 A gas chromatograph, equipped with a methylsilicone capillary column (30 m × 0.32 mm) and a flame ionization detector.

Recycling Procedure

After complete conversion of the substrate, the products were extracted at 50 °C by successive liquid-liquid extractions and decantations with heptane until all organic compounds had been removed from the hydrogel phase (monitoring by GC analysis). Residual heptane was removed under vacuum. The hydrogel-embedded Ru colloidal suspension could then be reused.

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