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Polymer catalyst with self-assembled hierarchical access for sortable catalysis

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ABSTRACT

This study aimed at the present challenge in self-controlled catalysis, addressing how to furnish the catalysts with sortable catalytic ability. This objective was reached by developing a polymer catalyst made of metal nanoparticles and a unique polymer carrier containing self-assembled hierarchical access. The hierarchical access, by closing, relaxing and opening, acted as a molecular switch for providing sequenced entrance to the encapsulated metal nanoparticles. This polymer catalyst showed poor catalytic reactivity at relatively low temperatures due to the closed access, which blocked substrate from the encapsulated metal nanoparticles. This polymer catalyst showed, however, significant reactivity for small molecules of substrate at modest temperatures, arising from relaxing of the access, which allowed small molecules to gain entrance to the catalytic metal nanoparticles. This polymer catalyst further showed significant reactivity for large molecules of substrate at relatively high temperatures, in response to the opening at the access. In this way, this polymer catalyst demonstrated the sortable catalytic ability. This suggested protocol opens up the opportunity to develop smart catalysts for controlled chemical processes.

1. Introduction

Despite the fascinating prospect in chemical synthesis and in inaccessible sites, self-controlled catalysis remains still a significant challenge. A remarkable achievement made in this field would be the use of smart polymer catalysts to achieve tunable catalytic ability [1,2]. From the earliest successes, exemplified by poly(*N*-isopropylacrylamide) (PNIPAm)-encapsulated metal nanoparticles [3,4], smart polymer catalysts have been demonstrating tunable catalytic ability in water. This can be related to the thermosensitive hydrophilic/hydrophobic transition at PNIPAm, which leads to either impeded or unobstructed access into the encapsulated metal nanoparticles. In this way, catalysis by the smart polymer catalysts shows a tunable process. The level of innovative thinking applied to develop smart polymer catalysts over the years has been high. This may be reflected by the adoption of special polymers or polymeric materials containing elaborate structures as the support of metal nanoparticles, such as hydrogels, core–shell microspheres and functional nanoparticles [5–7]. Nonetheless, the development of polymer catalysts with sophisticated self-controlled ability has been proven to be difficult, mainly because most of the practical catalytic processes involve multi-component reactants and multi-reaction processes [8–10]. These complicated reaction processes often desire the polymer catalysts that have sortable catalytic ability and that can distinguish two or more chemical processes. Unfortunately, it is out of reach for acquiring such polymer catalysts basing on currently reported results and methods. As such, new methods and technology are urged.

The creation of specified structures with desired properties and functions has been the fundamental mission at chemical and material sciences. Nature, as the best example of the smart systems, promotes scientists to seek aspirations by its self-assembled ability, functionality and self-adapted ability. A body of knowledge is already available. One of these is the recognition of synergistic interactions at biopolymers [11,12], which appears to provide a promising prospect for the development of hierarchically controlled ability. Consisting of various amino acids that involve in a broad spectrum of interactions and particularly non-covalent interactions, including hydrogen bonds, electrostatic forces, π–π stacking, host–guest interactions, *etc*, the biopolymers (such as protein) can form ordered self-assembled architectures that automatically adapt to the change of environments. The reason behind this can be ascribed to the synergy among these interactions, where the relatively stronger interactions may greater dictate the polymeric conformations yet the weaker interactions provide cooperation. In this manner, the synergy among these interactions endows the polymer with environment's adaptability. A rapid

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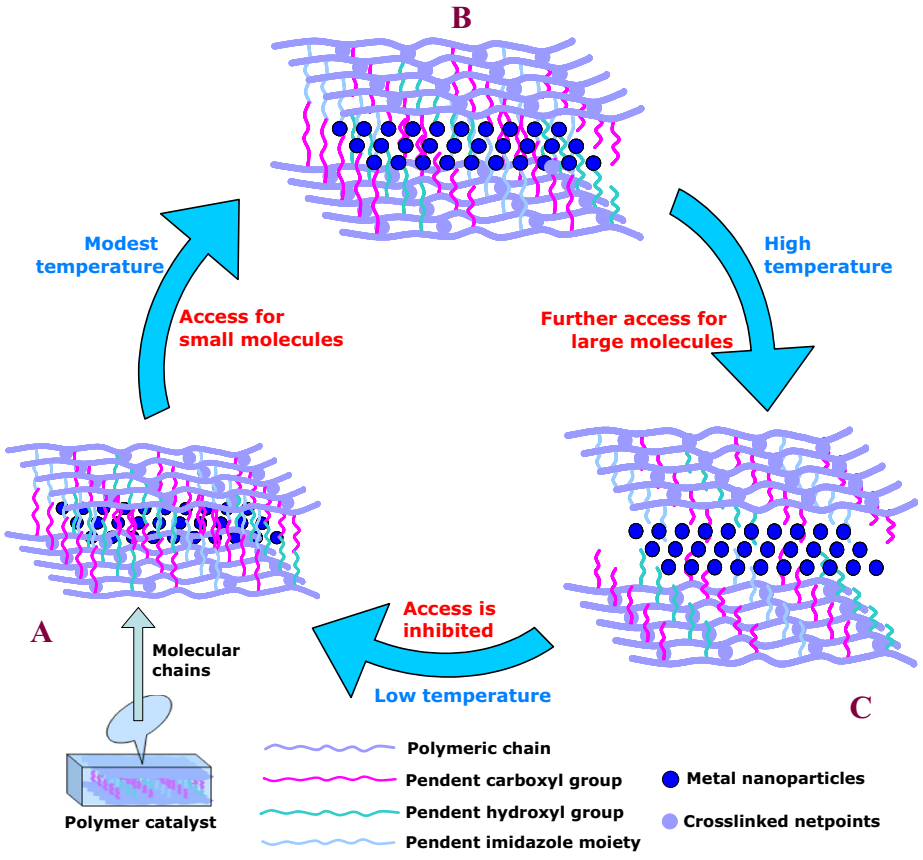
change in the environment would induce a sequenced dissociation/association at these interactions, resulting in hierarchical switching of the polymeric conformations. The switching behavior is reversible due to the reversibility of these non-covalent interactions. In this way, the synergy among these interactions allows for the occurrence of hierarchically controlled behaviors. Although these reported works are not related to catalytic applications, the synergistic manner at biopolymers provides a new insight into the struggling polymer catalysts, which makes feasible hierarchical access.

Inspired by this principle, herein we aimed at the present challenge in self-controlled catalysis by developing a novel polymer catalyst, which was furnished with self-assembled hierarchical access capable of sortable catalytic ability. This polymer catalyst (named "AgPC-HCS") was constructed from Ag nanoparticles and a unique polymer carrier containing self-assembled access made of two different interactions, that is, weak hydrogen bonds (between PPol and PTFMA) and relatively stronger polymer complexes (between PVI and PTFMA) (PPol: poly(4-penten-1-ol); PVI: poly(1-vinylimidazole); PTFMA: poly(2-trifluoromethylacrylic acid). The self-assembled access acts as a molecular switch for providing sequenced access to the encapsulated metal nanoparticles. As proposed in Scheme 1, the closed access in this polymer catalyst at relatively low temperatures would block substrate from the encapsulated metal nanoparticles, resulting in poor catalytic reactivity (Status *A*). The access for small molecules of substrate is, however, allowed with increasing temperature, arising from disrupting of these hydrogen-bonding interactions (Status *B*). The access may be further opened for a bigger molecule at relatively high temperatures, resulting from the dissociation of the PVI–PTFMA complexes (Status *C*). The switching behavior is reversible due to the reversibility of these non-covalent interactions. In this way, the self-assembled hierarchical access allows for the occurrence of the sortable catalytic ability. To that end, methylene blue (MB) and 2-nitrophenol (NPh) were selected as the tentative substrates, given their difference in molecular sizes (MB much larger than NPh, with 319.9 and 139.1 in molar mass, respectively) and the fact that their reductions with borohydride compounds are the common model reactions in catalytic test [13,14]. The objective of this study is to demonstrate that polymer catalysts having sortable catalytic ability can be prepared by using this novel protocol, which opens up the opportunity to develop smart catalysts for controlled chemical processes.

2. Experimental section

2.1. Preparation of polymer catalysts

Unless otherwise noted, the chemicals used were of analytic grade and used as received from Sigma–Aldrich. The polymer catalyst, as outlined in Scheme 1, was prepared basing on the suggested optimization for interpolymer complexes [15] and would be further discussed afterward, where the functional monomers 2-trifluoromethylacrylic acid (TFMA), 4-penten-1-ol (Pol) and 1-vinylimidazole (VI) were used in a stoichiometric molar ratio to ensure the entire complexation between carboxyl groups and both hydroxyl and imidazole moieties. In detail, stoichiometric Pol/TFMA complexes (Pol: 0.27 g; 3.19 mmol) and VI/TFMA complexes (VI: 0.28 g; 3.0 mmol) were dissolved in dimethylsulfoxide



Scheme 1. Proposed mechanism for the AgPC-HCS catalyst.