Polyacrylamide-based Functional Polymer-immobilized Perruthenate for Aerobic Alcohol Oxidation

Hiromi Hamamoto, Masahiro Kudoh, Hideyo Takahashi, Hideaki Natsugari, and Shiro Ikegami*
School of Pharmaceutical Sciences, Teikyo University, Sagamiko, Tsukui-gun, Kanagawa 199-0195

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A novel polymer-bound perruthenate catalyst for aerobic oxidation was designed utilizing poly(*N*-isopropylacrylamide) (PNIPAAm). The catalyst is highly effective to oxidize primary alcohols into aldehydes and can be reused without any significant loss of catalytic activity.

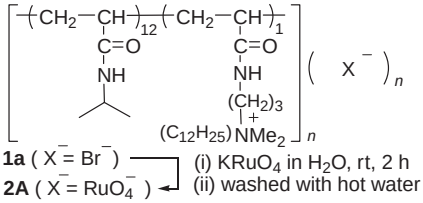
Because of the significant advantages over homogeneous catalysts such as ease of recovery and recycling, atom utility, and enhanced stability, solid-supported (heterogeneous) catalysts have gained increasing attention in the last few years.[1–3] The development of heterogeneous catalytic oxidation systems that use molecular oxygen as a primary oxidant, which is readily available and produces water as the sole by-product, is of paramount importance.[4–7] Many attempts have been directed toward the heterogenization of soluble catalytic species, and various supports with differing physical properties have been explored. The use of inorganic supports, such as hydroxyapatite, microporous zeolite, mesoporous silica, etc., is effective in the creation of recyclable aerobic oxidation systems.[6] In contrast, examples of metal catalysts supported on functional polymers for aerobic oxidation are still limited, even though they may possess multifunctional advantages and could allow material applications.[3,7]

Poly(*N*-isopropylacrylamide)[PNIPAAm]-based polymers have intrinsically temperature-responsive behavior and undergo thermally reversible changes between water-soluble and -insoluble states across a lower critical solution temperature.[8,9] Owing to this unique characteristic, they have been applied in various fields such as drug-delivery systems, actuators, and separation devices.[10]

In the course of our research on the utilization of PNIPAAm as a catalyst support material, PNIPAAm-bound catalyst was found to be useful in the development of recyclable oxidation systems.[11,12] We report here a novel design of a PNIPAAm-bound ruthenium catalyst developed for use in conjunction with molecular oxygen.

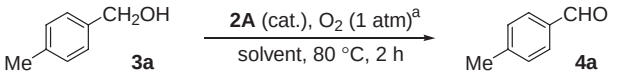
Ruthenium complexes have great potential for the catalytic oxidation reaction of various compounds.[13,14] Among the ruthenium complexes, the perruthenate ion shows promising catalytic properties for various oxidative transformations. Tetrapropylammonium perruthenate alone is an active catalyst for the oxidation of alcohols if the water can be removed in situ by adding activated molecular sieves to the reaction system. Although the use of a polystyrene-based resin yielded polymer-bound perruthenate,[7b] it is still quite difficult to recycle, possibly due to oxidative degradation of the polymer support.[15]

Previously, we investigated the self-assembly of the water-soluble PNIPAAm polymer with an inorganic species and found that the resulting complexes work as an efficient and stable solid-phase catalyst of oxidation reactions.[11,12] Scheme 1 shows the preparation of the PNIPAAm-bound ruthenium catalyst



Scheme 1.

Table 1. Oxidation of **3a** with molecular oxygen catalyzed by **2A**



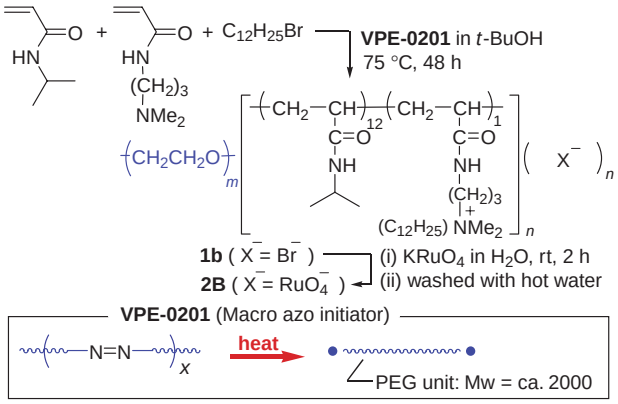
Entry	**2A**/mol %	Condition	Solvent	Additive	Conv./%[b]
1	5	O_2	$PhCH_3$	—	44
2	2	O_2	$PhCF_3$	—	65
3	2	O_2	$PhCF_3$	4A MS	68
4	2	O_2	$PhCF_3$	H_2O[c]	39

[a]O_2 balloon. [b]Determined by gas chromatographic analysis. [c]Solvent ($PhCF_3$) was saturated with H_2O.

following the previous procedure.[11a] A solution of **1a** in water was mixed with aqueous potassium perruthenate solution to afford ruthenium catalyst **2A** (81%) as an insoluble complex. The **2A** thus prepared was utilized in the oxidation of 4-methylbenzyl alcohol (**3a**) with molecular oxygen. The yields were insufficient even though **2A** was applicable in this oxidation (Table 1, Entries 1 and 2). In general, the ruthenium(VII)-catalyzed reaction requires 4A molecular sieves to avoid deactivation, possibly due to the water generation in the oxidation process. However, the addition of 4A molecular sieves to this heterogeneous system did not improve reactivity (Entry 3). The low yield observed in the wet solvent condition indicated that the presence of water in this system diminished its catalytic activity (Entry 4).

In search of a better oxidation catalyst for aerobic oxidation, a polyethylene glycol (PEG) block co-polymer containing the PNIPAAm ruthenium catalyst was newly designed. PEG-based or PEG-containing polymers have often been used in the construction of efficient oxidation systems.[7c,16] Moreover, a hydrophilic PEG component might act as a temporary water absorption unit from the catalytic site in an identical phase at high temperature because the temperature-responsive behavior[8,9] of PNIPAAm gel forms a hydrophobic environment, while the holding water would be released after cooling due to the loss of hydrophobicity on the PNIPAAm chain.

The PEG block-containing PNIPAAm chain **1b** was easily prepared using the azo compound 4,4′-azobis(4-cyanovaleric acid)–PEG copolymer (VPE-0201[17]) as a polymerization initiator. Subsequent complexation with perruthenate in water afford-



Scheme 2.

Table 2. Oxidation of **3a** with molecular oxygen catalyzed by **2B**

Entry	**2B**/mol %	Condition	Solvent	Additive	Conv./%[b]
1	5	O_2	$PhCH_3$	—	>95
2	2	O_2	$PhCF_3$	—	>95
3	2	Air	$PhCF_3$	—	95
4	2	O_2	$PhCF_3$	H_2O[c]	90

[a]O_2 balloon. [b]Determined by gas chromatographic analysis. [c]Solvent ($PhCF_3$) was saturated with H_2O.

ed the new polymer-bound ruthenium catalyst **2B** (Scheme 2[17]).

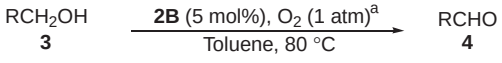
In the **2B**-catalyzed oxidation of **3a** with 1 atm of molecular oxygen, greater catalytic activities were observed compared with the original PEG block-free PNIPAAm ruthenium catalyst (Table 1, Entries 1 and 2, vs Table 2, Entries 1 and 2). In addition, the catalytic activity was less affected by the presence of water in the solvent and oxidation proceeded smoothly even under an air atmosphere instead of pure molecular oxygen (Table 2, Entries 3 and 4).

The scope of utilization of the **2B**-catalyzed oxidation system for a wide variety of primary alcohols was examined in toluene. Oxidation proceeded efficiently to give the corresponding aldehydes, as summarized in Table 3.

Furthermore, the catalyst could be recovered by simple filtration and reused without significant loss of activity (Scheme 3). Ruthenium leaching in the filtrate was negligible (estimated from ICP-MS analysis: 0.000016%).

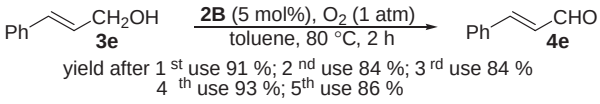
In summary, we developed a polymer-supported ruthenium

Table 3. Aerobic oxidation promoted by **2B** in toluene



Entry	Substrate	Product	Yield/%[a]
1[b]	4-$ClC_6H_4CH_2OH$ (**3b**)	4-ClC_6H_4CHO (**4b**)	90
2[b]	4-$CH_3OC_6H_4CH_2OH$ (**3c**)	4-$CH_3OC_6H_4CHO$ (**4c**)	89
3[b]	4-$NO_2C_6H_4CH_2OH$ (**3d**)	4-$NO_2C_6H_4CHO$ (**4d**)	88
4[b]	$PhCH{=}CHCH_2OH$ (**3e**)	$PhCH{=}CHCHO$ (**4e**)	91
5[c]	Geraniol (**3f**)	Citral (**4f**)	87
6[c]	Farnesol (**3g**)	Farnesal (**4g**)	65
7[c]	Octanol (**3h**)	Octanal (**4h**)	82
8[d]	$Ph(CH_2)_2CH_2OH$ (**3i**)	$Ph(CH_2)_2CHO$ (**4i**)	76

[a]Yield of isolated product. [b]Reaction time: 2 h. [c]Reaction time: 6 h. [d]Air (1 atm), reaction time: 12 h.



Scheme 3.

catalyst and demonstrated its efficiency in aerobic oxidation. The utility of the PNIPAAm version of a heterogeneous catalyst and ease of catalyst preparation may offer multifunctional advantages in both further modifications and applications. In addition, the results described here will enhance the utility of PNIPAAm polymers in the field of organic synthesis. More detailed investigations into the roles of the PEG unit in this system are currently ongoing.

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