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RESEARCH PAPER

Esterification of Phosphoric Acid with Equimolar Lauryl Alcohol Catalyzed by a Schiff Base Manganese Complex Anchored to a Keggin Heteropolyacid

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Abstract: Inorganic-organic hybrids were prepared by combining Schiff base complexes of manganese with silicotungstic acid (SiW). The composition and structure of the hybrid L^1-Mn-SiW (L^1: *N,N'*-disalicylidene-1,6-hexanediamine) were characterized by infrared spectroscopy and thermogravimetry. They were used as solid catalysts in the esterification of phosphoric acid with equimolar lauryl alcohol to monoalkyl phosphate ester (MAP). Over the L^1-Mn-SiW catalyst, the yield and selectivity for MAP were 93% and > 98%, respectively, at the optimal reaction conditions. The catalyst exhibited excellent recoverability during a six-cycle test without any observable change of the catalyst structure. A base-catalyzed reaction route was proposed.

Key words: heteropolyacid; Schiff base; inorganic-organic hybrid catalyst; phosphoric acid; lauryl alcohol; esterification; monoalkyl phosphate ester

Monoalkyl phosphate esters of long-chain alkyl alcohols (MAP) are important raw materials for manufacturing antistatic agents, emulsifiers, and wetting agents [1,2]. MAP is currently produced by the reaction of phosphoric anhydride or polyphosphoric acid with an alcohol without a catalyst [1,3]. This process suffers from the use of phosphoric acid, low chemoselectivity due to the formation of phosphoric acid diesters, and difficulty in purifying the MAP product [1–3]. Therefore, it is desirable to synthesize MAP by a green process, i.e., the condensation of equimolar amounts of phosphoric acid and alcohol over a highly efficient and recyclable heterogeneous catalyst with water as the sole by-product [1,4]. Sathe et al. [5] found that silica chloride (SiO_2-Cl) gave a high catalytic activity in the synthesis of phosphate ester with an excess amount of alcohol in the reaction medium. Dueymes et al. [6] observed considerable yields of phosphoric acid monoesters when acetic anhydride was used to activate an inorganic phosphate for the conversion of low carbon alcohols. Sakakura et al. [7–9] reported extremely active oxorhenium-(VII) complexes and/or nucleophilic bases with good selectivity for MAP. However, these catalysts have the disadvantages of high cost and the difficulty of their separation from the reaction medium. To find new catalysts with high activity coupled with convenient recoverability and stable reusability remains a challenge.

It is known that heteropolyacids (HPAs) are widely used as catalysts in various acid-catalyzed reactions, such as esterification, etherification, and hydration of olefins, because of their unique properties of strong Brönsted acidity and "pseudoliquid behavior" [10]. On the other hand, the use of a Schiff base and its metal complexes as catalysts for organic reactions has attracted much attention during the past two decades, which may

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be attributed to the variety of available structures and high thermal stability [11]. The combination of Schiff base compounds with HPAs can give novel inorganic-organic hybrid materials, in which a strong electrostatic or coordinate interaction between the organometallic cationic species and the polyoxometalate (POM) anions may bring about exciting synergistic effects to promote catalytic activity. Only a few examples of these hybrid materials have been investigated as catalysts for oxidation reactions [12–14], e.g., a Fe(salen)-POM hybrid catalyst showed a high catalytic activity in the oxidation of hydrocarbons [12].

Recently, we designed and prepared several inorganic-organic hybrid catalysts by introducing organic blocks into heteropolyanion units and found that they had high catalytic activity in redox and acid-catalyzed reactions [15–18]. In this work, the anchoring of the Schiff base complexes of manganese (L-Mn, L: *N*,*N*′-disalicylidene-1,6-hexanediamine (L^1), *N*,*N*′-disalicylidene-ethanediamine (L^2), or *N*,*N*′-disalicylidene-1,2-phenylenediamine (L^3)) onto silicotungstic acid ($H_4SiW_{12}O_{40}$, abbreviated as SiW) was used to prepare several solid hybrid catalysts. We observed that L^1-Mn-SiW can catalyze a green heterogeneous esterification process of phosphoric acid with equimolar lauryl alcohol by a base-catalyzed reaction, in which the new catalyst gave a high yield and selectivity for MAP and showed easy recoverability and stable reusability.

1 Experimental

1.1 Preparation of the catalysts

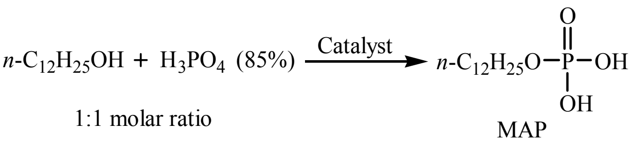
The Schiff base ligands L^1, L^2, and L^3 were prepared by the method reported in the literature [19]. The Schiff base Mn(III) complexes L^1-Mn, L^2-Mn, and L^3-Mn (Scheme 1) were prepared using a 1:1 molar ratio of the Schiff base (L^1, L^2, or L^3) to $MnCl_2\cdot 4H_2O$ in the synthesis mixture. The hybrid catalysts L^1-Mn-SiW, L^2-Mn-SiW, and L^3-Mn-SiW were prepared using a 2:1 molar ratio of the resulting complex (L^1-Mn, L^2-Mn, or L^3-Mn) to $H_4SiW_{12}O_{40}$ in the next synthesis procedure. The sample L^1-Mn-SiW is used here as an example to describe the detailed procedure. L^1 (2 mmol) was dissolved in 40.0 ml ethanol, and $MnCl_2\cdot 4H_2O$ (2 mmol) was added to the above solution at room temperature under stirring for 2 h with the formation of a dark green precipitate. This was recovered by filtration and washed with a mixture of ethanol and water. The resulting solid (L^1-Mn, 2 mmol) was dissolved in 40.0 ml methanol, into which SiW (1 mmol) was added, followed by stirring of the light green slurry for 6 h. The final solid product (0.61 g) was obtained by filtration, washing with a mixture of ethanol and water, and drying at 80 °C for 12 h in a vacuum oven. The sample L^1-Mn-SiW$^{\#}$ was the product prepared with a 1:1 molar ratio of L^1-Mn to SiW following the same synthesis procedure based on 2 mmol L^1. The weight of the product obtained was 0.62 g.

1.2 Characterization of the catalysts

The thermogravimetry (TG) analysis experiment was conducted on a Netzsch STA409 thermal analyzer in a mixture of N_2 and O_2 at a heating rate of 10 °C/min. Disc samples for Fourier transform infrared spectroscopy (FT-IR) were pressed from the powdered catalysts with dried KBr. The spectra were recorded using a Thermo Nicolet NEXUS spectrometer.

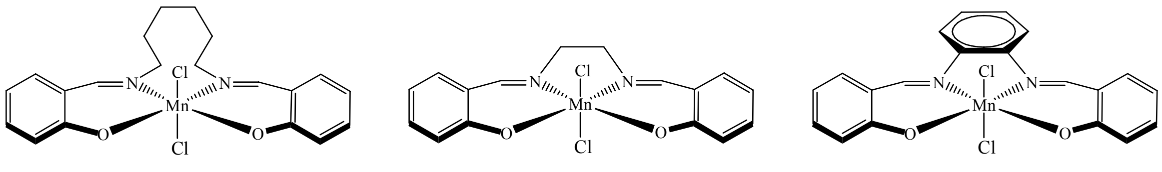
1.3 General procedure for esterification

The esterification of phosphoric acid with equimolar lauryl alcohol (Scheme 2) was carried out in a 100 ml three-necked round-bottomed flask. The powder L^1-Mn-SiW catalyst (0.10 g, 0.027 mmol), phosphoric acid (0.10 mol, 85% aqueous solution), and lauryl alcohol (0.10 mol) were charged into the flask, and the mixture was heated at 90 °C for 1 h under stirring. For comparing the catalysts, no solvent was used. After that, the reaction temperature and the amount of catalyst and solvent were changed to optimize reaction conditions using the catalyst L^1-Mn-SiW. The yield and selectivity of MAP in the product mixture were determined by potentiometric titration based on the amount of phosphoric acid in the starting reactants with the three different dissociation constants of H_3PO_4. Two



$$n\text{-}C_{12}H_{25}OH + H_3PO_4\ (85\%) \xrightarrow{\text{Catalyst}} n\text{-}C_{12}H_{25}O{-}\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle OH}{|}}{P}}{-}OH$$

Scheme 2. Esterification of phosphoric acid with equimolar lauryl alcohol into MAP.



L^1-Mn L^2-Mn L^3-Mn

Scheme 1. Structure of the Schiff base Mn(III) complexes of L^1-Mn, L^2-Mn, and L^3-Mn.

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