Hydrothermal Synthesis of Ruthenium-Substituted Heteropolyanion, $[SiW_{11}O_{39}Ru(III)(H_2O)]^{5-}$ as a Water Soluble Oxidation Catalyst

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(Received June 17, 1999; CL-990519)

Tris(acetylacetonate)ruthenium, $Ru(acac)_3$, successfully reacts with the lacunary heteropolyoxometalate, $K_8[SiW_{11}O_{39}]$ under hydrothermal conditions (6 MPa nitrogen at 200 ℃), to give the mono-substituted heteropolyanion, $[SiW_{11}O_{39}Ru(III)(H_2O)]^{5-}$. The heteropolyanion shows notable activity on the air oxidation of alkylaromatics at 200 ℃ in water as solvent.

Many kinds of transition metal-substituted heteropolyanions, $XW_{11}O_{39}M^{n-}$ where X = Ni, Fe, Co, Mn, Ru, Ce, etc. and M = P, Si, have been synthesized and characterized.[1] The Ru-substituted heteropolytungstosilicate anion, $[SiW_{11}O_{39}Ru(III)(H_2O)]^{5-}$, **1**, is normally synthesized from a salt of lacunary heteropolytungstate, α-Keggin-$K_8SiW_{11}O_{39}$, **2**, and a commercial ruthenium chloride, $RuCl_3 \cdot nH_2O$.[2] In some recent reviews and references,[1,3] isolated **1** has been referred to as (i) an electrochemically inactive Ru complex, and (ii) a mixture of several isomers. On the other hand, the cesium salt of the corresponding tungstophosphate, $Cs_4[PW_{11}O_{39}Ru(III)(H_2O)]$, **3**, was isolated in the pure form and well characterized, indicating that the direct electrochemical oxidation of Ru actually succeeded; well-defined redox waves corresponding to Ru were readily observed by cyclic voltammetry (CV).[3b,4] It appears to be quite difficult to obtain the pure anion, **1**, with high yield from $RuCl_3 \cdot nH_2O$, because it is a complicated and variable mixture of mono- or polymeric Ru, where their oxidation states are three and four.[5] An alternative procedure started from $[Ru(II)(H_2O)_6](C_7H_7SO_3)_2$, which is mixed with the lacunary anions followed by oxidation with molecular oxygen. However, this method was reported to also be unsuitable for obtaining **1**.[3b] Although the modified method using a cation exchange-resin has been applied to improve the purity,[6] an optimized method for the synthesis of **1** still seems to be needed.

This paper describes that the hydrothermal method is a very effective and practical method for the synthesis of **1** using $Ru(acac)_3$ as the Ru source, which has been chosen because its oxidation state is definitely three and it is also a commercially available compound. Hydrothermal synthesis was carried out as follows: $Ru(acac)_3$ (0.73 mmol), $K_8[\alpha\text{-}SiW_{11}O_{39}] \cdot 14H_2O$ (0.73 mmol)[7] and 45 ml deaerated water was poured into a 70ml autoclave and purged with nitrogen at 6 MPa. The reaction was carried out at 200 ℃ for 2 h. The same procedure was conducted using commercial $RuCl_3 \cdot nH_2O$ (n=1-3) as a comparison. After the reaction, homogenous black solutions, which are stable for more than several months, are obtained in both cases. Any unreacted $Ru(acac)_3$ was not extracted by an organic solvent. The absorption spectrum of the solution suggested the formation of different Ru complexes. In $RuCl_3 \cdot nH_2O$ as the Ru source, the spectrum at *ca.* 430 nm (ε = 4180 $dm^3\ mol^{-1}\ cm^{-1}$) was assigned to the Ru interacted with the heteropolyanion as shown in Figure 1. No specific peaks for the Ru were observed when $Ru(acac)_3$ was used for the hydrothermal reaction. In comparison, $Ru(acac)_3$ was treated with **2** in water under reflux conditions for 2 h. Although some $Ru(acac)_3$ was dissolved in hot water, the spectrum indicated that mostly soluble Ru still remained as acetylacetonate complex without any reaction with **2** even under reflux conditions (see Figure I). As a result, the hydrothermal condition is an essential step to promote the reaction of $Ru(acac)_3$ with the lacunary heteropolyanion, **2**.

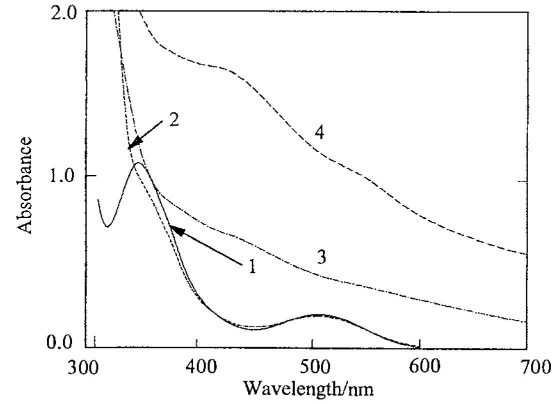

Figure 1. Absorption spectra. (1) $Ru(acac)_3$, (2) reflux sample of $Ru(acac)_3$ with $K_8SiW_{11}O_{39}$, (3 and 4) $Ru(acac)_3$ and $RuCl_3 \cdot nH_2O$ with $K_8SiW_{11}O_{39}$ after hydrothermal reaction, respectively.

In order to confirm the actual formation of the Ru-substituted heteropolyanion, the solution obtained from the hydrothermal method was diluted with KH_2PO_4 solution for adjusting the potassium concentration, 0.5 mol dm^{-3} and subjected to CV. Interestingly, in the case of $Ru(acac)_3$ as the Ru source, well-defined reversible redox couples of Ru at +0.78 V, +0.49 V, and -0.19 V (*vs.* Ag/AgCl in saturated NaCl) were observed corresponding to Ru(V/IV), Ru(IV/III) and Ru(III/II), respectively (Figure 2(a)). No redox waves for impurities of the Ru ion were observed. The cyclic voltammogram shows a totally different Ru redox potential with respect to previous data.[8] The electro-oxidation of Ru(III) to Ru(IV) at +0.695 V was possible with a quantitative charge of 1.0 F mol^{-1} without any Ru deposits by bulk-electrolysis. This suggests that all of the acetylacetonate ligand was completely exchanged by the inorganic heteropolyanion ligands and Ru^{3+} was incorporated into the heteropolyanion.

These potentials of Ru(V/IV) and Ru(III/II) were apparently *ca.* 0.15 V more negative than those observed for the corresponding tungstophosphate, **3**, in the pH range of 4.0-6.5.[3b]

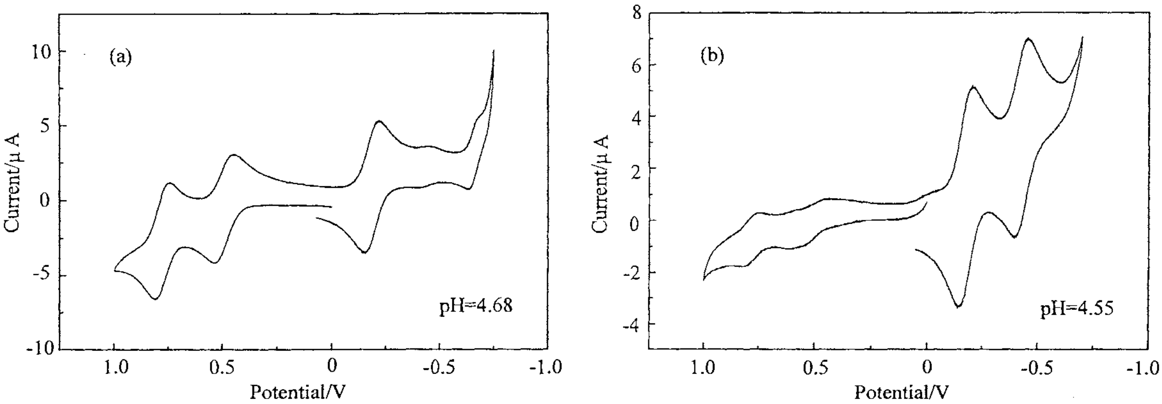

Figure 2. Cyclic voltammetry of 1.0mmol dm^{-3} Ru solution at a glassy carbon electrode. (a) $Ru(acac)_3$ and (b) $RuCl_3 \cdot nH_2O$ solution treated with $K_8SiW_{11}O_{39}$ under hydrothermal condition, respectively. Sweep rate 20 mV s^{-1}.

Thus, the redox potential of the incorporated Ru has found to be affected by the heteroatom of the polyanion. The shift in the redox potential probably depends on the negative charge density of the lacunary heteropolytungstate anion. Interestingly, when the same experiment was carried out using $RuCl_3 \cdot nH_2O$ instead of $Ru(acac)_3$, the observed redox waves of Ru were complicated and very weak (Figure 2(b)). It is noteworthy that two redox couples at -0.17 and -0.43 V were almost similar to those observed for the corresponding parent heteropolyanion, $[SiW_{12}O_{40}]^{4-}$. These waves were ascribed to the one-electron redox process of W (VI/V).[9] However, a preliminary experiment showed that the saturated polyanion was not capable of keeping Ru homogenous and $RuCl_3 \cdot nH_2O$ easily gave Ru deposits without lacunary polyanion under hydrothermal conditions. These results suggested that the lacunary polyanion did not change to the parent polyanion in the presence of $RuCl_3 \cdot nH_2O$. Although the interpretation of the cyclic voltammogram is still ambiguous, this seems to be caused by the unsuccessful incorporation of Ru into the polyanion.

The isolation of **1** as a salt from the hydrothermal solution using $Ru(acac)_3$ was carried out. The black powder was easily isolated as the cesium salt by salting out. Recrystallization of the powder in water gave a black crystal (yield: 0.78 g, *ca.*30%). The elemental analysis (Anal.Found: Cs; 18.7, Si; 0.81, W; 54.9, Ru; 2.6, H_2O; 3.7%. Calcd: Cs; 18.5, Si; 0.78, W; 56.4, Ru; 2.8, H_2O; 4.0%)[10] and FT-IR spectrum, which shows the typical Keggin structure (Figure 3), confirms that the structure is $Cs_5[SiW_{11}O_{39}Ru(III)(H_2O)] \cdot 7H_2O$. Three reversible redox waves of the Ru in the isolated complex showed the same result of the solution treated under hydrothermal conditions as shown in Figure 2(a). Black powder was also obtained when $RuCl_3 \cdot nH_2O$ was used, however, the elemental analysis and CV of the compound were not successful. Excess amounts of Ru which had not been incorporated into heteropolyanion were detected in the powder.

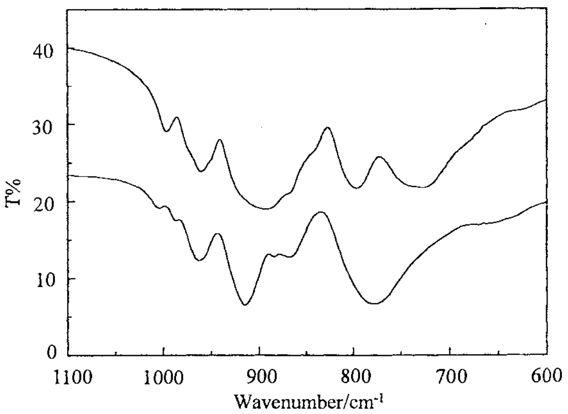

Figure 3. FT-IR spectra. Top: $K_8[SiW_{11}O_{39}]$, bottom: $Cs_5[SiW_{11}O_{39}Ru(H_2O)]$.

Interestingly, $Cs_5[SiW_{11}O_{39}Ru(III)(H_2O)] \cdot 7H_2O$ showed high activity on the oxidation of alkylaromatic compounds in water as solvent. As a typical example, *p*-xylene (0.79 mmol) was oxygenated with the heteropoly compound (0.019 mmol) in water (7.5 ml) using an autoclave with magnetic stirring at 200 ℃ under 6 MPa of air. After 5 h, 99% of *p*-xylene was converted to terephtalic acid(58.8%), *p*-toluic acid(17.6%), *p*-toluic aldehyde(0.2%), and carbon dioxide(20%) as the sole byproduct. It is noteworthy that the oxidation activity is also observed even when $RuCl_3 \cdot nH_2O$ and **2** were used as catalyst without isolation of the complex.[11] Identification of the active species is now progress. As a result, the Ru-substituted heteropolyanion is a notable example of a "green oxidation catalyst" in a non-halogen containing water solvent system.

References and Notes

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10 Ruthenium and silicon were analyzed by inductively coupled plasma (ICP), tungsten by X-ray fluorescence, and cesium by atomic absorption. Water was determined using Karl Fischer's reagent.
11 For example, $RuCl_3 \cdot nH_2O$ (0.092 mmol) and **2** (0.092 mmol) were used for the oxidation of *p*-xylene (4 mmol) to give terephtalic acid (44.2%), *p*-toluic acid (9.2%), *p*-toluic aldehyde (0.15%) and carbon dioxide (8.5%) after 2h under the same conditions.