Heterogeneous ruthenium catalysts supported on an organic-inorganic material derived from iron-oxidizing bacteria: Catalytic hydration of nitriles

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Abstract: Hydration of organonitriles to organoamides is one of the most important transformation for valuable chemicals. The most successful example of the research area is a biocatalytic transformation of acrylonitrile to acrylamide. One of the most effective central metal of homogeneous catalysts is ruthenium. We have been investigated highly active homogeneous ruthenium catalysts.

We developed a new type of the heterogeneous ruthenium catalysts. Iron-oxidizing bacteria, *Leptothrix* species produce microtubular organic–inorganic materials that encase the bacterial cells. We succeeded to prepare new ruthenium containing materials from the microtubular materials. The structure and catalytic behavior of the new ruthenium materials will be presented.

Keywords: ruthenium catalysis, hydration of nitrile, heterogeneous catalysis

1. Introduction

Heterogeneous catalysts have some advantages for industrial production of chemicals. Among them, heterogeneous ruthenium catalysts widely used in hydrogenation of unsaturated organic molecules. We have been investigated homogeneous ruthenium catalysis for dehydrogenation of 1,4-butanediol[1] and hydration of nitriles for about 20 years. Our next interest was directed to a heterogeneous ruthenium catalysis. It would be interesting to compare the heterogeneous ruthenium catalysis with our homogeneous ruthenium catalysis system.[2]

Our new heterogeneous catalyst was prepared from a product produced from iron-oxidizing bacteria. The color of the bacteria is orange to brown. We can find this type of color at a creek, a paddy field, and a fountain form a groundwater. A microscopic image of the bacteria is shown in Figure 1A. The iron-oxidizing bacteria contains many species, so called *Leptothrix*. The *Leptothrix* is a generic name. The bacteria produce a characteristic material. TEM images of the materials are shown in Figure 1B. They have tube like structure or this type of ribbon structure.

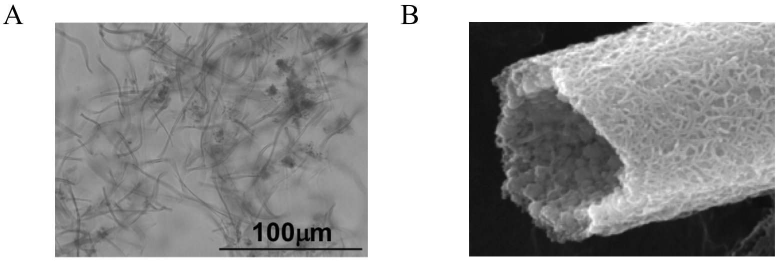


Figure 1. Microscopic image of the iron-oxidizing bacteria (A) and TEM images of the materials produced by the bacteria (B).

The tubular material is an organic and inorganic hybrid material. The organic component is polysaccharide, and the inorganic part contains iron, silicon, and phosphorus. These elements are derived from underground water. Iron and silicon are absorbed on the organic tubular skeleton. Moreover, it has a wide surface area about 280m^2/g.[3] These features seem to be a suitable for a support of a heterogeneous catalyst.

We succeeded to prepare new ruthenium heterogeneous catalysts from the microtubular materials by newly developed two-stage process.

2. Experimental

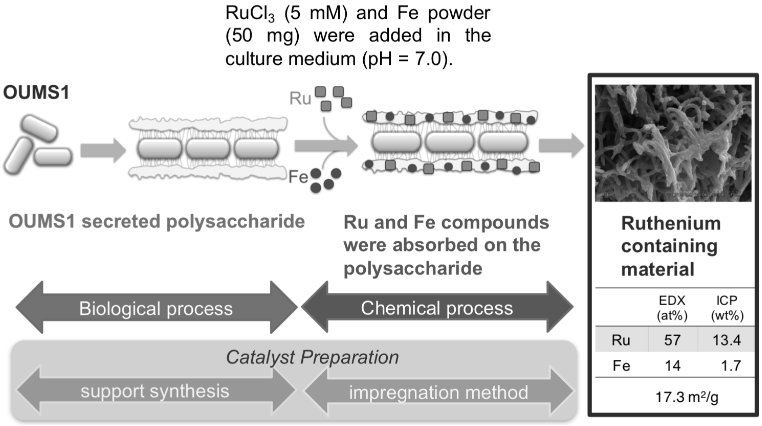
The isolated *Leptothrix*, OUMS1, is cultured by the method described in the literature.[4] After formation of tubular materials, $RuCl_3 \cdot 3H_2O$ and iron metal were added to the culture medium under pH 7.

Prepared ruthenium catalysts were analyzed by XRD, TEM, and XPS. Catalytic reactions were performed in a sealed glass tube. Products were analyzed by gas chromatography and ^1H NMR.

3. Results and discussion

The *Leptothrix* contains many species. We isolated single species, iron-oxidizing bacteria, form a mixture of *Leptothrix*. We named the isolated species OUMS1.[4] The reason for the isolation is to ensure reproducibility of our experiments and to do a chemical modification of the microtubular materials. Artificial multiplication of OUMS1 for heterogeneous catalyst, will be able to control a chemical composition of the product. We wanted to prepare a ruthenium containing material given OUMS1's help, however, OUMS1 died when ruthenium source was added to a culture medium. Ruthenium ion was a toxic chemical for OUMS1.

Finally, we developed two-stage hybrid process (Figure 2). The first stage is a biological process and the second stage is a chemical process. In the first stage, OUMS1 produced tubular polysaccharide. The polysaccharide is a skeleton. After the formation of the polysaccharide tube, $RuCl_3 \cdot 3H_2O$ and iron metal were added in the culture medium. At room temperature under atmospheric pressure, ruthenium and iron compounds were absorbed on the organic tube. A form of the obtained material is like a rod, not a tube.



	EDX (at%)	ICP (wt%)
Ru	57	13.4
Fe	14	1.7
17.3 m²/g		

Figure 2. Preparation of a heterogeneous ruthenium catalyst.

The obtained ruthenium containing materials acted as a catalyst for hydration of nitriles. Several nitriles tested converted to the corresponding amides in water at 180 °C for 24 h in good yields. The catalyst was air stable and the reaction proceeded in the air. In addition, the catalyst was able to reuse.

XPS analysis showed that Ru(III) species adsorbed on polysaccharide surface and a nitrogen atom of the galactosamine in polysaccharide coordinated to the Ru(III) center. Amorphous nature of the catalyst was revealed by XRD and electron diffraction analysis. Comparison of a catalytic behavior of the heterogeneous catalyst with our homogeneous ruthenium catalysts will be discussed.

4. Conclusions

The new heterogeneous ruthenium catalyst was prepared by two-stage hybrid process, biological and chemical process using isolated pure iron-oxidizing bacteria. The catalyst proceeded the hydration reaction in water under neutral conditions.

References

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