





N. Mizuno

The author presented on this page has published more than **25 articles** since 2000 in Angewandte Chemie, most recently: "A Highly Active Protonated Tetranuclear Peroxotungstate for Oxidation with Hydrogen Peroxide": R. Ishimoto, K. Kamata, N. Mizuno, Angew. Chem. **2012**, 124, 4740–4743; Angew. Chem. Int. Ed. **2012**, 51, 4662–4665.

## Noritaka Mizuno

**Date of birth**: August 3, 1957

**Position**: Professor, Department of Applied Chemistry, School of Engineering, The University of Tokyo

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Education: 1980 BEng with Prof. Yukio Yoneda, The University of Tokyo

1982 MEng with Prof. Makoto Misono, The University of Tokyo 1985 PhD with Prof. Makoto Misono, The University of Tokyo 1985–1989 Research Associate, The University of Tokyo

1989 Postdoctoral fellow with Prof. Richard G. Finke, University of Oregon (USA)

Awards: 2006 Nissan Science Award; 2008 GSCN Green and Sustainable Chemistry Award; 2009 Hattori

Hoko Award; 2010 Catalysis Society of Japan Award

Current research Design and synthesis of novel polyoxometalates (POMs); POM-based heterogeneous catalysts;

interests: nanostructured macrocation-POM complexes; development of supported catalysts

**Hobbies**: Fishing and reading mystery novels

My mottos are ... "be naïve" and "be creative".

My favorite way to spend a holiday is ... fishing in a mountain stream.

When I was eighteen I wanted to be ... an adventurer because I wanted to explore the unexplored (so, I am a chemist).

f I could be described as an animal it would be ... a Japanese Shiba dog. I am faithful to my master (i.e., my wife).

The biggest challenge facing scientists is ... development of efficient methods for energy conversion, in particular an artificial photosynthetic system.

Chemistry is fun because ... we can synthesize materials at the atomic and/or molecular levels.

Young people should study chemistry because ... it is indispensable for improving the quality of our lives, exploring nature, and realizing our dreams.

My favorite drink is ... champagne.

My first experiment were ... acidity measurements of mixed oxides by IR spectroscopy.

n a spare hour, I ... am an omnivorous reader of research papers in all chemistry fields.

f I could be any age I would be ... 22 years old. It would be interesting to choose a totally different research area.

admire ... my wife's patience with me.

The secret of being a successful scientist is ... to have a self-critical eye and to have the luck to work with talented co-workers.

**M**y favorite molecule is ... a polyoxometalate, in particular  $[\gamma-SiW_{10}O_{36}]^8-$ .

If I had one year of paid leave I would ... study something other than chemistry, perhaps biology or physics.

f I could be a piece of lab equipment, I would be ... an NMR machine or X-ray diffractometer because I like to guess the compositions and structures of materials.

The most important thing I learned from my students is ... to keep my mind younger.

The principal aspect of my personality is ... "que sera sera".

What I appreciate most about my friends is ... that they give me a different point of view.

My favorite painter is ... Pablo Picasso.



## How has your approach to chemistry research changed since the start of your career?

At the beginning of my career, our research group was engaged in the development of heterogeneous catalysts (in particular for gas-phase reactions) by the one-person-one-project approach. Since I was promoted to full professor, our research group has grown in terms of the number of group members, and many co-workers have joined from various fields such as inorganic, organic, complex, materials, and electrochemistry. Now, we can do various kinds of projects with many talented members who have different chemical backgrounds and skills. For example, we have successfully designed highly active heterogeneous catalysts by using our knowledge of complex chemistry, and also device materials by using our skills in inorganic and organic synthesis.

## My 5 top papers:

- 1. "Highly Efficient Utilization of Hydrogen Peroxide for Selective Oxygenation of Alkanes Catalyzed by Diiron-Substituted Polyoxometalate Precursor": N. Mizuno, C. Nozaki, I. Kiyoto, M. Misono, J. Am. Chem. Soc. 1998, 120, 9267 - 9272.
  - By using the lacunary silicodecatungstate [γ-SiW<sub>10</sub>O<sub>36</sub>]<sup>8</sup> as a "structural motif", we synthesized several metal-substituted POMs ("molecular catalysts") with controlled active sites by introducing metal cations (e.g., Fe, V, Cu, Mn, Ti, Zn, Al, Zr, Hf, Y, Pd) into the vacant sites. This was our first paper on catalysis by a dimetal-substituted  $\gamma$ -Keggin POM.
- 2. "A Breathing Ionic Crystal Displaying Selective Binding of Small Alcohols and Nitriles: K<sub>2</sub>[Cr<sub>3</sub>O(OOCH)<sub>6</sub>- $(H_2O)_3][\alpha\text{-SiW}_{12}O_{40}]\cdot 16\,H_2O$ ": S. Uchida, M. Hashimoto, N. Mizuno, Angew. Chem. 2002, 114, 2938-2941; Angew. Chem. Int. Ed. 2002, 41, 2814-2817.
  - Complexation of polyoxometalates with macrocations and monovalent cations forms compounds with controlled channel sizes, channel volumes, and guest affinities. It is expected that 1) anionic POM charges control the channel volumes, 2) carbon chain lengths of the bridging ligands of macrocations control the hydrophilicity/hydrophobicity of the channels, and use of aromatic species as terminal ligands regulates arrangements of constituent ions by  $\pi - \pi$  stacking, and 3) electronic configurations of monovalent cations control the guest affinities. This was our first paper on the synthesis and sorption properties of a macrocation-POM complex.
- 3. "Supported Ruthenium Catalyst for the Heterogeneous Oxidation of Alcohols with Molecular Oxygen": K. Yamaguchi, N. Mizuno, Angew. Chem. 2002, 114, 4720-4724; Angew. Chem. Int. Ed. 2002, 41, 4538-4542.

During the course of our investigations on the design of POM-based molecular catalysts, we found that various

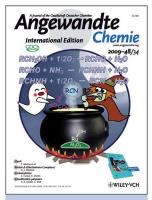
## How do you think your field of research will evolve over the next 10 years?

I have been active in polyoxometalate (POM) chemistry since I was a student. Over the past few decades, this field has developed explosively. POMs are a large family of anionic metal-oxygen clusters that are thermally and oxidatively stable. Their chemical and physical properties, such as redox potentials, (multi)electron-transfer properties, acidities, solubilities, and negative charges, can finely be tuned by choosing the constituent elements and countercations. Now, POM chemistry has become a key emerging area to create "molecular-based materials". Perhaps over the next ten years, many new types of molecular-based catalysts (including heterogeneous catalysts) and devices (e.g., storage batteries), and hopefully even an artificial photosynthetic system will be developed.

- functional group transformations should be promoted by the "concerted activation" of substrates by the Lewis acidic and Brønsted basic sites of metal hydroxides. This was our first paper on catalysis by a supported metal hydroxide. We have subsequently developed efficient heterogeneous catalysts for many green functional-group transformations.
- "Efficient Epoxidation of Olefins with ≥99% Selectivity and Use of Hydrogen Peroxide": K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, Science 2003, 300, 964-966.
  - We synthesized a novel lacunary silicodecatung state [γ- $SiW_{10}O_{34}(H_2O)_2$ <sup>4-</sup> that can catalyze the epoxidation of olefins with  $\geq$  99% selectivity with respect to epoxide and >99% efficiency of H<sub>2</sub>O<sub>2</sub> utilization. From the results in this paper, we came up with an idea to design tungsten-based catalysts for oxygenation with H<sub>2</sub>O<sub>2</sub>. To date, we have synthesized various novel tungstenbased catalysts such as a diperoxotungsten dimer, a selenium-bridged diperoxotungsten dimer, and an Sshaped silicodecatungstate dimer for the atom-efficient oxidation of alkenes, silanes, and sulfides.
- "Zinc(II) Containing γ-Keggin Sandwich-Type Silicotungstate: Synthesis in Organic Media and Oxidation Catalysis": Y. Kikukawa, K. Yamaguchi, N. Mizuno, Angew. Chem. 2010, 122, 6232-6236; Angew. Chem. Int. Ed. 2010, 49, 6096-6100.

We developed new procedures for the synthesis of metal-substituted POMs in organic media by using appropriate lacunary precursors with which the isomerization and decomposition of the original lacunary frameworks can be completely avoided. This finding made the design of well-defined active sites with POMs much easier, and various molecular catalysts, which could not be synthesized in aqueous media, have been synthesized.

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The work of N. Mizuno has been featured on the cover of Angewandte Chemie: "Catalytic Oxidative Synthesis of Nitriles Directly from Primary Alcohols and Ammonia": T. Oishi, K. Yamaguchi, N. Mizuno, Angew. Chem. 2009, 121, 6404-6406; Angew. Chem. Int. Ed. 2009, 48, 6286-6288.