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ENZYMATIC CATALYTIC PERFORMANCE OF CLUSTER CATALYSTS OF ZINC, COBALT AND MANGANESE FOR TRANSESTERIFICATION AND AMIDE ALCOHOLYSIS

Mardi 28 mars 2017 à 16h
Salle D2

Biographie

Kazushi Mashima received his PhD degree (1986) from Osaka University. He became an Assistant Professor at Institute for Molecular Science, Okazaki National Institutes in 1983 before getting his PhD degree. He moved to Faculty of Engineering, Kyoto University as an Assistant Professor in 1989, and then to Faculty of Science, Osaka University as an Assistant Professor in 1991. He worked as a post-doctoral fellowship with Professor M. A. Bennett, Australian National University in 1992 and as an Alexander von Humboldt fellow with Professor W. A. Herrmann, Technische Universität München in 1993. He was promoted to an Associate Professor at Faculty (now Graduate School) of Engineering Science, Osaka University in 1994, and then to a full Professor at Graduate School of Engineering Science, Osaka University in 2003. He received Progress Award in Synthetic Organic Chemistry, Japan in 1994, BCSJ Award in 2000, The Chemical Society of Japan Award for Creative Work for 2008, The 9th Green and Sustainable Chemistry Award in 2010, and The Award of the Society of Polymer Science, Japan in 2010.

His current research interests lie in the area of organometallic chemistry for metal-catalyzed organic transformations, including direct amination of alcoholic substrates, asymmetric hydrogenation, and polymerization catalysis as well as

Abstract:

The ester moiety represents one of the most ubiquitous functional groups in organic compounds, serving as both key intermediate and protecting group in organic transformations. Among various esterification reactions established so far, one of the most convenient synthetic methods is transesterification, in which methyl or ethyl esters react with various alcohols to give the corresponding esters in one step. We developed μ -oxo-tetranuclear zinc cluster $Zn_4(OCOCF_3)_6O$ as an efficiently catalyst for transesterification, including chemoselective acylation of hydroxy group in the presence of aliphatic amino group, catalytic acetylation of alcohols and catalytic deacetylation of acetates. Because of mildness of the reaction conditions, these reactions have a high degree of functional-group tolerance. Recently, cobalt and manganese clusters mediate the same chemoselectivity for transesterification. Amide bond formation and degradation are also discussed.

(1) Studies of the Electronic Effect of Zinc Cluster Catalysts and Their Application to the Transesterification of β -Keto Esters.

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Yuji Nishii, Shoko Akiyama, Yusuke Kita, Kazushi Mashima, *Synlett*, 26, 1831-1834 (2015).

(3) Enzyme-like Catalysis via Ternary-Complex Mechanism: Alkoxy-bridged Dinuclear Cobalt Complex Mediates Chemoselective O-Esterification over N-Amidation.

Yukiko Hayashi, Stefano Santoro, Yuki Azuma, Fahmi Himo, Takashi Ohshima, and Kazushi Mashima, *J. Am. Chem. Soc.*, 135, 6192-6199 (2013).

(4) Zinc-Catalysed Amide Cleaved Esterification of β -Hydroxyethylamides.

Yusuke Kita, Yuji Nishii, Takafumi Higuchi, and Kazushi Mashima, *Angew. Chem. Int. Ed.*, 51, 5723-5726 (2012).

(5) Sodium Methoxide: a simple but highly efficient catalyst for the direct amidation of esters.

Takashi Ohshima, Yukiko Hayashi, Kazushi Agura, Yuka Fujii, Asako Yoshiyama, and Kazushi Mashima, *Chem. Commun.*, 48, 5434-5436 (2012).

(6) Additive Effect of N-Heteroaromatics on Transesterification Catalyzed by Tetranuclear Zinc Cluster.

Y. Maegawa, Y. Hayashi, T. Iwasaki, T. Ohshima, and K. Mashima, *ACS Catalysis*, 1, 1178-1182 (2011).

(7) A Tetranuclear Zinc Cluster-Catalyzed Practical and Versatile Deprotection of Acetates and Benzoates.

T. Iwasaki, K. Agura, Y. Maegawa, Y. Hayashi, T. Ohshima, and K. Mashima, *Chem. Eur. J.*, 16, 11567-11571 (2010).

(8) Enzyme-Like Chemoselective Acylation of Alcohols in the Presence of Amines Catalyzed by a Tetranuclear Zinc Cluster.

T. Ohshima, T. Iwasaki, Y. Maegawa, A. Yoshiyama, and K. Mashima, *J. Am. Chem. Soc.*, 130, 2944-2945 (2008); Highlighted in *Nature*, 452, 415-416 (2008); *Science*, 319, 1163 (2008).