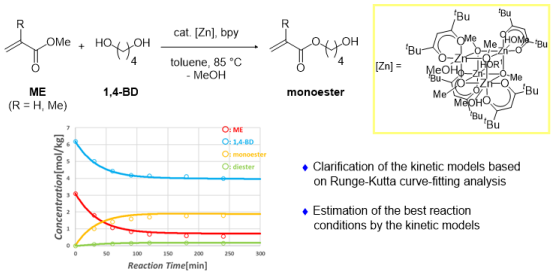
Kinetic analysis for optimizing the Zn-catalyzed transesterification conditions of MA and MMA with diols to maximize monoesterified products

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Innovation and Business Development Division, Nippon Shokubai Co., LTD.*) ○Taito KATO,[1,2] Haruki NAGAE,[1] Kazushi MASHIMA[1]

Keywords: (Meth)acrylates; Diols; Transesterification; Kinetic analysis; Cluster complexes

(Meth)acrylate is widely used in industrial products, and terminal hydroxylated (meth)acrylates are monomers directly produced by diols and methyl (meth)acrylate, but catalytic transesterification, which is an equilibrium reaction that selectively and highly converts mono-esterification, requires well-optimized reaction conditions. Catalytic transesterification, however, involves several obstacles that must be overcome, such as (1) a long reaction time to proceed to transesterification, (2) a statistical mixture of terminal hydroxylated monomers and diol bis(meth)acrylates, and (3) contamination by undesired side reactions, such as Michael addition and polymerization of vinyl monomers.

In this study, we demonstrated that a unique alkoxy-bridged tetranuclear zinc complex $[Zn(tmhd)(OMe)(MeOH)]_4$ worked as an appropriate catalyst for the transesterification of methyl (meth)acrylate with a variety of diols such as 1,4-butanediol, briefly leading to an equilibrium state of a statistical mixture of the terminal hydroxylated monomers and diol bis(meth)acrylates.[1] The zinc complex also minimized an undesired influence of side reactions such as Michael addition and polymerization in the case of methyl acrylate. We also report that the yield of terminal hydroxylated monomers was maximized on the basis of an in-depth kinetic study based on the Runge-Kutta method curve-fitting analysis using Mathcad software. DFT calculations of the reaction mechanism of methyl acrylate and 1,4-butanediol suggested that the transesterification was preferentially catalyzed by a mononuclear zinc catalyst compared with a dinuclear zinc species, and the activation energy of the first step of the transesterification precisely matched the result of the curve fitting analysis.



1) T. Kato, S. Akebi, H. Nagae, K. Yonehara, T. Oku, K. Mashima, *Catal. Sci. Technol.*, **2021**, *11*, 6975–6986.

© The Chemical Society of Japan