Supplementary Information for

Kinetic Analysis of Aqueous-phase Cyclodehydration of 1,4-Butanediol and Erythritol over a Layered Niobium Molybdate Solid Acid

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Mass transfer limitation

In the liquid-phase reaction, it is necessary to ascertain that no mass transfer limitations occur. For the highest reaction rates, mass transfer calculations were carried out. The Weisz-Prater criterion is useful to judge the absence of the internal diffusion limitations.

$$C_{WP} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{AS}} < 1 \qquad (11)$$

In this equation, $-r'_{A(obs)}$ is the observed reaction rate [kmol/kg-cat·s], ρ_c is the solid catalyst density [kg/m^3], R is the catalyst particle radius [m], and C_{AS} is the concentration of substrate A at the catalyst surface [kmol-A/m^3]. Also, D_e is the effective diffusivity [m^2/s], which is equal to $(D_{AB}\ \varphi_p\ \sigma_c)/\tau$ where D_{AB} is the diffusivity [m^2/s], φ_p is the catalyst porosity [-], σ_c is the constriction factor [-], and τ is the tortuosity [-]. For cyclodehydration of 1,4-butanediol, the highest reaction rates over $HNbMoO_6$, Amberlyst-15 and H-ZSM5, $-r'_{A(obs)}$, were 6.9×10^{-6}, 6.4×10^{-6} and 3.6×10^{-6} [kmol/kg-cat·s], respectively. Other quantities for the three catalysts are listed in Table S1. The concentration C_{AS} and diffusivity D_{AB} of 1,4-butanediol were 3.3 [kmol/m^3] and 5×10^{-9} [m^2/s].[S1] The values of C_{wp} were calculated to be 2.6×10^{-3}, 1.3×10^{-2} and 3.6×10^{-3} for $HNbMoO_6$, Amberlyst-15 and H-ZSM5, respectively. For the case of cyclodehydration of erythritol, the values of C_{wp} were obtained to be 3.9×10^{-4}, 1.9×10^{-3} and 6.0×10^{-4} for $HNbMoO_6$, Amberlyst-15 and H-ZSM5, respectively. Since these values are <<1, internal mass transfer effects can be neglected.

Table S1 Quantities used for estimation of the Weisz-Prater Criterion in the three catalysts

Catalyst	Particle radius, R /m	Density, ρ_c /kg m^{-3}	Porosity, φ_p	Constriction factor, σ_c	Tortuosity, τ
$HNbMoO_6$	5×10^6	1.0×10^3	0.4[a]	1	1
Amberlyst-15	5×10^6	1.2×10^3	0.32	0.8[a]	3.0[a]
H-ZSM5	5×10^6	0.7×10^3	0.4[a]	0.8[a]	3.0[a]

[a] Typical values of porosity, constriction factor and tortuosity are 0.4, 0.8 and 3.0, respectively.[S2] These values were used.

[References]

[S1] T. Tominaga and S. Matsumoto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 533.

[S2] H.S. Fogler, "Elements of Chemical Reaction Engineering", Pearson Education Inc., 2010, p.816.