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Innovation in a chemical reaction process using a supercritical water microreaction system: environmentally friendly production of ε-caprolactam

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Our microreaction system using supercritical water solutions achieves nearly 100% yield and 100% selectivity for ε-caprolactam production at reaction times shorter than 1 s.

The Beckmann rearrangement of cyclohexanone oxime into ε-caprolactam is one of the most industrially important acid-catalyzed reactions, which is the starting monomer for the production of nylon 6. However, its practical production has suffered from serious disadvantages of using environmentally damaging catalysts such as highly concentrated sulfuric acid and of forming large quantities of valueless by-products such as ammonium sulfate, about twice as much as the product by weight. The use of heterogeneous catalysts as an environmentally friendly alternative has been limited so far, because of problems such as the low selectivity to ε-caprolactam as well as short catalyst life.[1]

Supercritical water (scH_2O) should be a useful replacement for organic solvents because water is the most environmentally acceptable and inexpensive solvent, and its physicochemical properties can be changed widely with density. However, the ionic product (K_w) for scH_2O is much lower than that of liquid water,[2] and there is almost no research work on the use of scH_2O as a catalyst for acid-catalyzed organic syntheses.[3] According to the K_w concept, such reactions have been undertaken in hot water below 573 K,[4] but the reaction rates are relatively slow. We tried the Beckmann rearrangement using scH_2O in a batchwise operation;[5] however, the observed yields were very far from satisfactory for practical purposes. Contrary to the conventional wisdom that acid-catalyzed reactions will be difficult to rapidly proceed in scH_2O, we have still predicted acceleration of the organic synthesis by using scH_2O, based on our finding on the significant reduction of the strength of hydrogen bonding near the critical point.[6] We demonstrate that our microreaction (μ-reaction) system can achieve high selectivity in satisfactory yield for ε-caprolactam production even in the absence of any acids.

The scH_2O μ-reaction system can heat up reacting species very quickly to the supercritical state and then can quench them rapidly to room temperature after the reaction, and can exclude the influence of the region of hot water on the way to the supercritical state. Furthermore, the decrease in linear dimensions provides very large surface to volume ratios as well as very good heat- and mass-transfer conditions, which avoid hot spots inside the reactor, leading to the possibilities of eliminating unwanted side reactions and of promoting desired reactions.[7] As shown in Fig. 1, the scH_2O solution heated up to around 773 K was sent to the entrance of a quick-heating part (union tee made of Hastelloy C-276) through a 1/16 inch Hastelloy C-276 tube, while a stream of ambient cyclohexanone oxime aqueous solution (0.35 mol kg^{-1}) passing through a 1/16 inch Hastelloy C-276 tube was struck against the high-speed flow of the scH_2O in the union tee, and was found to heat up to 648 K within 0.05 s. The mixture was then introduced into a 50 μL reactor (250 μm i.d.) made of Hastelloy C-276, in which the reaction times were adjusted to be shorter than 1 s. After the reaction, the solution was quenched rapidly to room temperature in order to prevent pyrolysis. In order to effect such a rapid heating and to prevent temperature changes from occurring upon the addition of the substrate, not only was the μ-system filled with glass wool lagging material, but the relatively faster flow rate of scH_2O was kept at $>3\times$ that of the substrate solution. The fluctuations in temperature were controlled to within ±0.1 K. Detailed analysis of the reaction mixture was performed by GC, LC-MS and NMR. The IR spectra of scH_2O were measured by high-pressure and high-temperature FTIR.[8]

As shown in Table 1, the ε-caprolactam was obtained in a selectivity of 99% or above when the reaction was performed with the scH_2O μ-reaction system. Although a very small amount (maximally about 1%) of 6-aminocaproic acid was produced as a by-product, it can be easily dehydrated into the desired ε-caprolactam. When the mixture was heated up to 643 K at a slower rate of 6 K s^{-1} in a batchwise operation, we obtained only 1.9% yield (ratio of ε-caprolactam formed per mole of cyclohexanone oxime) at a reaction time of 180 s at 673 K and 40 MPa, in which cyclohexanone, as the hydrolysis product of cyclohexanone oxime, was predominantly formed. Hence, the hydrolysis of cyclohexanone oxime in the hot water region on the way to the supercritical state is presumed to be responsible for the low yields. Hot water without the μ-reactor did not show any reactivities below 573 K at 40 MPa, but the introduction of the μ-reaction system in the same region of hot water reaction led to an increase in the yield at a shorter reaction time of 0.913 s. On the other hand, in the sH_2O μ-reaction system at 673 K and 40 MPa the yield was increased greatly up to 83% even at a short reaction time of 0.625 s, its yield being comparable or superior to those promoted by conc. H_2SO_4[9] or B_2O_3/Al_2O_3 catalyst.[10] We recognize that the μ-reaction system can prevent the hydrolysis from taking place in hot water and thereby can bring out more adequately the function of scH_2O itself as acid. ε-Caprolactam production by our scH_2O μ-reaction system has been thus proved to be very selective and rapid, though a relatively higher K_w for hot water is generally

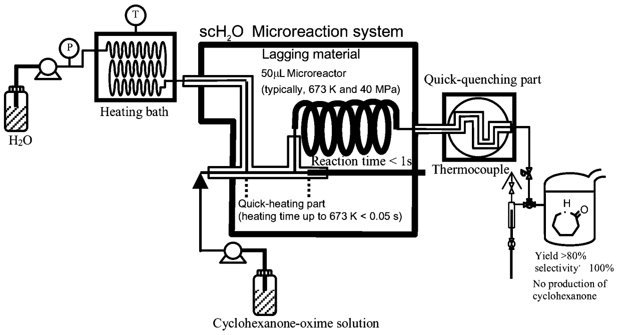

Fig. 1 A microreaction system for supercritical water, which has been applied to the rapid and selective production of ε-caprolactam.

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Table 1 The yields of ε-caprolactam production under various conditions

Reaction type	*T*/K	*P*/MPa	Reaction time/s	Selectivity (%)	Yield (%)
7.69 *m* conc. H_2SO_4 (ref. 9)	383	0.1	5400		72.0
B_2O_3(20%)/Al_2O_3 (ref. 10)	573	2.6×10^{-4}	5.65	75.0	72.0
high silica MFI zeolite (ref. 11)	623	0.1	3600	95.7	95.3
hot water[c]	523	40	180.0	0	0
hot water μ-reaction	573	40	0.913	100.0	9.5
scH_2O[c]	673	40	180.0	99.3	1.9
scH_2O μ-reaction	623	40	0.802	99.6	38.9
scH_2O μ-reaction	648	40	0.728	98.6	80.0
scH_2O μ-reaction	673	40	0.625	98.6	83.0
scH_2O μ-reaction	693	40	0.506	99.2	42.1
scH_2O μ-reaction	648	30	0.667	99.7	63.5
scH_2O μ-reaction	648	25	0.603	99.8	49.6
HCl scH_2O μ-reaction[a]	648	40	0.728	99.3	99.3
H_2SO_4 scH_2O μ-reaction[b]	648	40	0.728	99.5	99.5

[a] HCl concentration: 7.74×10^{-5} M (293 K, 0.1 MPa). [b] H_2SO_4 concentration: 2.46×10^{-4} M (293 K, 0.1 MPa). [c] Batchwise operation.

considered to serve in the place of conventional acids.[4] We further quantify the reaction efficiency, in which the rate of reaction is defined as the number of moles of ε-caprolactam formed per kilogram of solvent per unit time (in mol kg^{-1} h^{-1}). The rate of reaction with the scH_2O μ-reaction system at 673 K and 40 MPa reaches a high value of 549.5 mol kg^{-1} h^{-1} and is over 17000 times larger than in the batchwise operation, and what is more surprising, it is about 1100, 700, and 250 times larger than those obtained in 7.69 *m* (mol kg^{-1}) H_2SO_4[9] and in the vapor phase over B_2O_3(20%)/Al_2O_3[10] and high silica MFI zeolite,[11] respectively, which have been employed or are currently used for industrial production of ε-caprolactam.†

It is further noted that the yield in scH_2O becomes maximized at the near critical temperature at 40 MPa (Table 1). K_w monotonously decreases with increasing temperature in the near-critical region at 40 MPa, and the maximized yield is still not satisfactorily elucidated by the K_w concept alone. The change of hydrogen bonding is presumed to be a key factor for clarifying the specific temperature dependence. We observed the IR spectra of H_2O up to 743 K at 40 MPa (not shown). All spectra were normalized by the spectrum of H_2O at 298 K and 40 MPa. Fig. 2 shows the temperature dependence of the relative intensities of each species. The complete disappearance of the peak intensity assigned to the monomer and/or dimer structures around 3579–3756 cm^{-1} above 698 K indicates that the monomer and dimer concentrations above 698 K are small. It is well known[12] that the harmonic vibration of the bending mode, $2\nu_2$, is resonant with the dimer frequency assigned to the proton donor, ν_1 (= 3579 cm^{-1}), and the resonance peak should appear around 3620 cm^{-1}. As shown in Fig. 2, the Fermi resonance peak increases gradually with increasing temperature above 423 K up to the critical temperature, over which the intensity suddenly decreases, accompanied not only by the marked reduction of the bending mode above 653 K, but by a marked decrease in the dimer structures, and at or just above the critical temperature part of the dimer structure likely undergoes breakdown to H_3O^+ and OH^-.

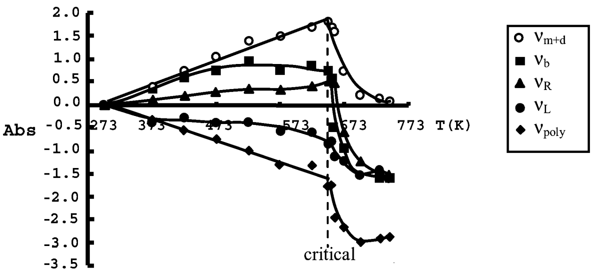

Fig. 2 The temperature dependence of the relative intensities of the frequencies assigned to species such as monomer and/or dimer structures (ν_{m+d}), bending mode (ν_b), out of plane bending mode (ν_L), Fermi resonance (ν_R) and hydrogen bonding network (ν_{poly}) at 40 MPa.

We further found that our μ-reaction approach enables the production of ε-caprolactam in more satisfactory yield by the addition of a very small amount of acid. As shown in Table 1, the addition of hydrochloric acid and sulfuric acid can increase the yield up to nearly 100% even at reaction times shorter than 1 s. To investigate the influence of increment [H$^+$] on the reactivities, we estimated the hydrogen ion concentrations of aqueous hydrochloric and sulfuric acids at 648 K and 40 MPa based on Sue′s model[13] and Xiang′s equation,[14] respectively. The concentrations of 7.74×10^{-5} M (293 K, 0.1 MPa) hydrochloric and 2.46×10^{-4} M (293 K, 0.1 MPa) sulfuric acid solutions correspond to 6.75×10^{-5} *m* and 7.55×10^{-6} *m*, respectively at 648 K and 40 MPa. Thus, the conversion into ε-caprolactam proceeds much more efficiently than expected by the estimated increment [H$^+$] with the addition of the dilute acids.

Notes and references

† Although the small size of the μ-reactors would seem to preclude industrial scale synthesis, it has been demonstrated that only a 50 μL reactor operating continuously in pure scH_2O at 40 MPa and 673 K could produce about 0.25 kg of ε-caprolactam in a day.

1 W. K. Bell and C. D. Chang, *US Pat.* 4,359,421, 1982.
2 W. L. Marshall and E. U. Franck, *J. Phys. Chem. Ref. Data*, 1981, **10**, 295.
3 T. Sato, G. Sekiguchi, T. Adschiri and K. Arai, *Chem. Commun.*, 2001, 1566.
4 For example, J. An, T. Bagnell, T. Gablewski and C. R. Strauss, *J. Org. Chem.*, 1997, **62**, 2505.
5 O. Sato, Y. Ikushima and T. Yokoyama, *J. Org. Chem.*, 1998, **63**, 9100.
6 Y. Ikushima, K. Hatakeda, N. Saito and M. Arai, *J. Chem. Phys.*, 1998, **108**, 5855.
7 S. J. Haswell, R. J. Middleton, B. O'Sullivan, V. Skelton, P. Watts and P. Styring, *Chem. Commun.*, 2001, 291.
8 Y. Ikushima, O. Sato, T. Yokoyama and M. Arai, *Angew. Chem., Int. Ed.*, 1999, **38**, 2910.
9 L. G. Donaruma and W. Z. Heldt, *Org. React.*, 1961, **11**, 1.
10 T. Curtin, J. B. McMonagle and B. K. Hodnett, *Appl. Catal. A: Gen.*, 1992, **93**, 75.
11 H. Ichihashi and H. Sato, *Appl. Cat. A: Gen.*, 2001, **221**, 359.
12 Y. Taniguchi, *Kinsekigai-Bunkoho*, Gakkai Shuppan Center, Tokyo, p.119.
13 K. Sue, Y. Hakuta, R. L. Smith, T. Adschiri and K. Arai, *Proc. 13th Int. Conf. on Properties of Water and Steam*, NRC Research Press, Ottawa, 2000, p. 145.
14 T. Xiang, K. P. Johnston, W. T. Wofford and E. F. Gloyna, *Ind. Eng. Chem. Res.*, 1996, **35**, 4788.