

ACCELERATION OF PROPYLENE HYDRATION NEAR THE CRITICAL TEMPERATURE OF WATER

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ABSTRACT

The hydration of propylene in the near-critical water was investigated using a flow reaction system. The hydration without catalysts was found to proceed in the temperature range between 300 and 400°. In the presence of 5.1×10^{-4} mol/kg sulfuric acid, the yield of IPA was increased greatly in the temperature range between 250 and 380°, indicating that the addition of a very small amount of sulfuric acid significantly accelerates the hydration reaction.

1. INTRODUCTION

The hydration of olefin to alcohol is a basic reaction in chemical industry. Isopropanol(IPA) is commercially produced by several hydration processes, in which some acid catalysts such as a solid phosphorous acid,^[1] an acidic ion exchange resin^[2] and a metal oxide^[3] have been used. Catalyst life for industrial applications is not long enough so that it is essential to regenerate and replace them or to treat acidic industrial effluent.

Water near the critical condition has interesting properties that differ from those under ordinary conditions. For example, the dielectric constant decreases with increasing temperature,^[4] and it behaves similar to a polar or a hydrophobic organic solvent. The ion product around 250° is about 1000 times larger than that at room temperature.^[5] In this region, it has been expected that some acid- or base-catalyzed reactions should readily proceed because of higher concentration of proton or hydroxide ion from water.^[6]

In view of these backgrounds, considerable efforts to use supercritical water in chemical syntheses have been made,^[7-15] and it has become clear that supercritical water is an

effective medium, a reactant and a catalyst. Thus, the hydration of olefin has also been investigated. Some hydration reactions using a zeolite catalyst,^[16] cyclohexene^[17] or carvone^[10] were reported. In this study we report the hydration of propylene using the near-critical water with and without a catalyst.

2. EXPERIMENTAL

We conducted the hydration at relatively lower water-to-propylene molar ratios for industrial applications under variable conditions to clarify the effects of temperature, pressure and residence time on the reactivity.

Figure 1 displays a schematic diagram of a flow reaction system for the hydration of propylene. Pure water (or aqueous dilute solution of sulfuric acid) was first preheated and then mixed with propylene just before the reactor. The reactor was 50 mL tube (2.18 mm ID, 3.18 mm OD, 13500 mm) made of Inconel 625 for reaction time of 10 min. The reactor effluent was cooled to room temperature through a condenser. After passing through a back-pressure regulator, gas and liquid samples were separately obtained.

We performed experiments in the following way. In the case of experiments without catalysts, the molar ratio of water to propylene was fixed at 30. Temperatures were ranged between 250 and 400? . Pressure and reaction time were 30 MPa and 10 min, respectively. When we used a catalyst, a dilute sulfuric acid(5.1×10^{-4} mol/kg) was employed instead of pure water, in which the molar ratio was 10. Temperatures were 280-380? . Pressure and reaction time were 30 MPa and 10 min, respectively. Water and propylene flow rates were calculated from the average density of a mixture of propylene and water at a certain reaction condition. Density of propylene was calculated by SRK equation,^[18] while that of water was available in the steam table.^[19]

The composition of samples was determined by a gas chromatograph equipped with a mass selective detector (GC-MS, Agilent technology model 5973N). A capillary column (liquid phase: HP-5, 60 m \times 0.25 mm \times 0.25 μ m, J&W) was used to separate into each pure component. The liquid sample included isopropanol and diisopropyl ether. The calibration standards were used to quantify the yield of each product. The composition of the gas stream which is composed of propylene and small amount of miner products, such as olefin isomers having six carbons(C6 olefins) and diisopropyl ether, was calculated on the basis of the area percentage.

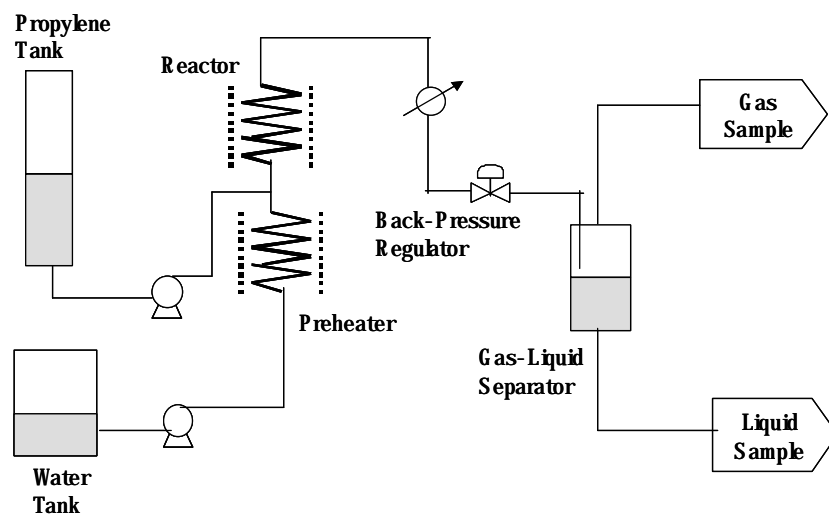


Figure 1
A schematic diagram of a flow reaction system for the hydration of propylene in supercritical water.

3. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the yield and the selectivity of IPA in the propylene hydration in the absence of catalysts, at a pressure of 30 MPa. The hydration of propylene was found to proceed in the temperature range between 300 and 400 °C, but we obtained only 4.0% yield.

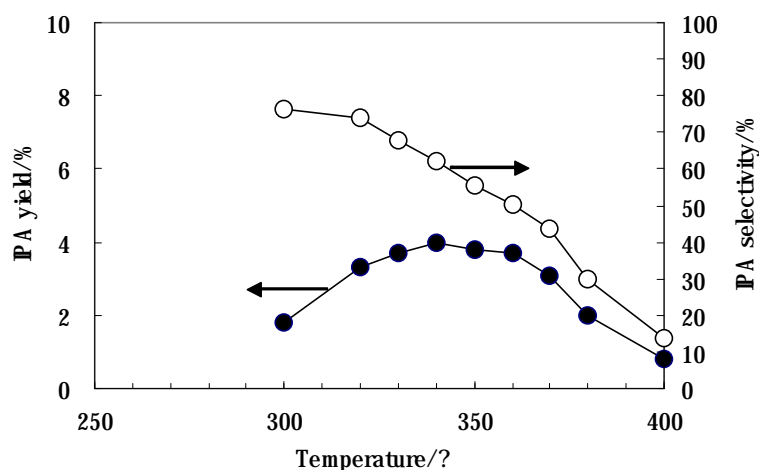


Figure 2
The temperature dependence of the yield of IPA (filled symbols) and the selectivity to IPA (open symbols) in the absence of catalysts at a reaction time of 10 min, pressure of 30 MPa and water-to-propylene molar ratio of 30.

The temperature dependence of the IPA yield showed a characteristic behavior. The yield increased with increasing temperature in the range of 300-340? , reaching a maximum at 340? , and then decreased. This temperature dependence might be explained by thermal energy and properties of water. At constant pressure of 30MPa the Kw values do not much change at 300-340? .^[5] Consequently, the ability of water to catalyze the hydration reaction do not much change, either. Hence the increase in the yield of IPA with temperature could be mainly due to thermal energy contribution. On the other hand, in the range of 340-400? the Kw values decrease significantly from -11.4 to -14.8, so water loses its ability to produce proton, resulting in decreasing the yield of IPA. In addition, an increase in the selectivity to C6 olefins with increasing temperature could indicate that a free radical species on behalf of ionic properties of water play an important role.

From the standpoint of industrial applications, IPA was not still obtained in a satisfactory yield in this noncatalytic hydration process. It seems natural that the low yield leads to costly process. Therefore, we attempted an improvement in the yield using a small amount of acid catalyst.

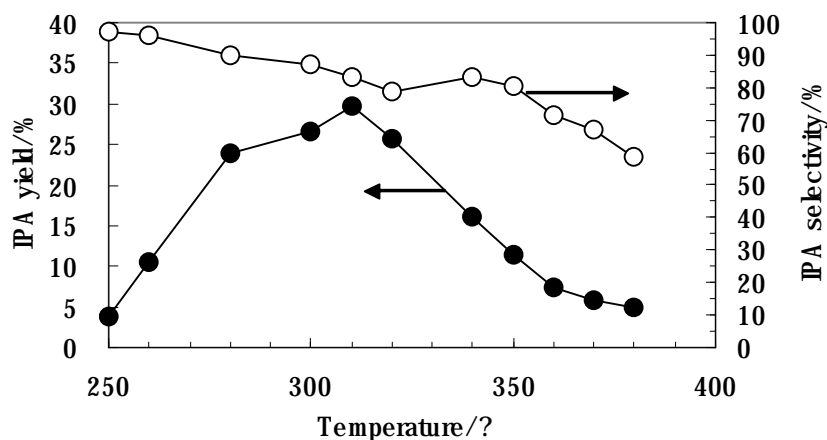


Figure 3

The temperature dependence of the yield of IPA (filled symbols) and the selectivity to IPA (open symbols) in the presence of dilute sulfuric acid (5.1×10^{-4}) at a reaction time of 10 min, pressure of 30 MPa and water-to-propylene molar ratio of 10.

Figure 3 shows the yield and the selectivity of IPA with temperature in the presence of 5.1×10^{-4} mol/kg sulfuric acid, at a pressure of 30 MPa. The yield of IPA was increased greatly in the temperature range between 250 and 380? , indicating that the addition of a very

small amount of sulfuric acid significantly accelerates the hydration reaction. The temperature dependence of the IPA yield was similar to that in the absence of catalysts. Hence it is also expected that the temperature dependence can be explained by thermal energy and water properties.

The reaction could be mainly accelerated by the proton being supplied by sulfuric acid. Thus, the reason for decreasing in the IPA yield at 310-380? should be concerned with the loss of catalytic activity of sulfuric acid. Under these conditions the dielectric constant is getting lower, and accordingly ionic properties of water are also getting smaller. Consequently, the dissociation of sulfuric acid is restrained.

4. CONCLUSION

The hydration reaction of propylene significantly proceeds in water near its critical temperature without any acid catalyst. The addition of a very small amount of sulfuric acid brings about a great increase in the IPA yield under these conditions. Although further investigation is essential to apply our method to a practical chemical process, our findings make us expect to realize these processes.

ACKNOWLEDGEMENTS

This study has been entrusted by NEDO (New Energy and Industrial Technology Development Organization). We thank for financial support.

REFERENCES

- [1] Japanese Patent JP51009728B, **1976**
- [2] Japanese Patent JP49117412, **1974**
- [3] EGUCHI, K., TOKIAI, T., KIMURA, Y., ARAI, H., Chem. Lett., **1986**, 567-570
- [4] UEMATSU, M., FRANK, E. U., J. Phys. Chem. Ref. Data, 9(4), **1980**, 1291-1306
- [5] MARSHALL, W. L., FRANCK, E. U., J. Phys. Chem. Ref. Data, 10(2), **1981**, 295-301
- [6] IKUSHIMA, Y., HATAKEDA, K., SAITO, N., ARAI, M., J. Chem. Phys., 108(14), **1998**, 5855-5860
- [7] SAVAGE, P. E., Chem. Rev., 99, **1999**, 603-621
- [8] CHANDLER, K., DENG, F., DILLOW, A. K., LIOTTA, C. L., ECKERT, C. A., Ind. Eng. Chem. Res., 36, **1997**, 5175-5179
- [9] KATRITZKY, A. R., ALLIN, S. M., Acc. Chem. Res., 29, **1996**, 399-406
- [10] AN, J., CABLEWSK, B. T., STRAUSS, C. R., TRAINOR, R. W., J. Org. Chem., 62, **1997**, 2505-2511
- [11] SATO, O., IKUSHIMA, Y., YOKOYAMA, T., J. Org. Chem., 63, **1998**, 9100-9102
- [12] IKUSHIMA, Y., SATO, O., SATO, M., HATAKEDA, K., ARAI, M., Chem. Eng. Sci., 58, **2003**, 935-941
- [13] IKUSHIMA, Y. et al., Chem. Commun., **2002**, 2208
- [14] IKUSHIMA, Y. et al., Chem. Eng. Sci., **2003**, 58, 935
- [15] TAKAHASHI, K., et al., Abstract of 17th International Symposium on Chemical Reaction Engineering (Hong Kong), **2002**
- [16] TOMITA, K., KODA, S., OSHIMA, Y., Ind. Eng. Chem. Res., 41, **2002**, 3341-3344
- [17] CRITTENDON, R. C., PARSONS, E. J., Organometallics, 13, **1994**, 2587-2591
- [18] The Society of Chemical Engineers, Japan, Kagakukougaku-binran, kaitei-6han, **1999**, 17-49
- [19] The Japan Society of Mechanical Engineers, Steam Tables, **1981**