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Vapor-phase Hydration of Dicyclopentadiene Catalyzed by Niobic Acid

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Vapor-phase hydration of dicyclopentadiene in a flow system was promoted by niobic acid. Maximum conversion to the hydrated product was obtained at around the boiling point of dicyclopentadiene, 170 °C. Niobic acid rapidly decreased its catalytic activity when it was heat-treated at temperatures higher than 300 °C.

Tricyclo[5,2,1,$0^{2,6}$]-3-decene-8(or 9)ol(DCPD-OH) has been used as a modifier for polyester or alkyd resin. It is prepared, in general, by a batchwise, or liquid-phase hydration of dicyclopentadiene(DCPD) in the presence of concentrated sulfuric acid.1) Recently it was reported that Nafion H, the acidic form of the polymeric fluorinated sulfuric acid, is effective to promote the hydration without corrosion and trouble of handling.2) However, there still remain some problems in the preparation process since Nafion is extremely expensive and the reaction is carried out only in a batchwise operation. It is prefered to prepare DCPD-OH by a vapor-phase reaction in a continuous operation at an ordinary pressure. On the other hand, niobic acid is recently found to be a prominent catalyst for vapor-phase hydration of ethylene.3) Hence, the vapor-phase hydration of DCPD catalyzed by niobic acid was attempted in this study.

Niobic acid(AD-460) supplied by CBMM Company was dried in air at 120 °C for 6 h, and heat-treated in air for 3 h at temperatures ranging from 200 to 500 °C. For comparison, catalytic activities of various metal oxides or mixed oxides and ion-exchange resins including Nafion H were examined. The metal oxides were prepared from respective metal alcoxides by neutralization using aqueous NH_3 solution. The mixed oxides were prepared by coprecipitation method from mixed solution of respective metal alcoxides. All metal oxides and mixed oxides were heat-treated at 400 or 500 °C immediately before use as a catalyst. Nafion H was prepared by acid-treatment of Nafion K, supplied by Mitsui-Du Pont Fluorochemicals Company, and used as a catalyst after drying in air at 120 °C for 1 h.

The vapor-phase hydration was performed at 120-220 °C in a conventional flow reactor at an ordinary pressure. A gaseous mixture of DCPD(11.8 vol%) and H_2O (88.2 vol%) was fed to the catalyst bed by using N_2 as a carrier gas. Unless otherwise noted, W/F(where W is the catalyst weight and F is the flow rate of the total reactants, DCPD plus H_2O) was kept at 5.9 $g \cdot h \cdot mol^{-1}$.

As is shown in Table 1, niobic acid heat-treated at 300 °C exhibited the highest catalytic activity among all the catalysts tested here. Succeeding to niobic acid, Nafion H showed fairly high catalytic activity immediately after use as a catalyst. However, its catalytic activity rapidly decreased with an elapse of reaction time and was almost lost possibly due to the coating of catalyst surface with an viscous product. On the other hand, the decrease in the catalytic activity of niobic acid was pronouncedly less compared to that observed for Nafion H. In addition, the activity was completely recovered by heat-treatment of the aged or deactivated niobic acid at 400 °C in air for 2 h.

The reaction temperature had a significant effect on the hydration as is exhibited in Fig.1 which shows the results of the reaction promoted by the niobic acid heat-treated at 300 °C. The catalyzed hydration was especially active at 170 °C, the boiling point of DCPD. It is known that DCPD is readily depolymerized or converted to cyclopentadiene by heat-treatment at temperatures higher than its boiling point.4) Thus, the result shown in Fig.1 suggests that the hydration may proceed favorably(as following) at the upper limit temperature permitting the existence of the double bond in the bicycloheptene ring.

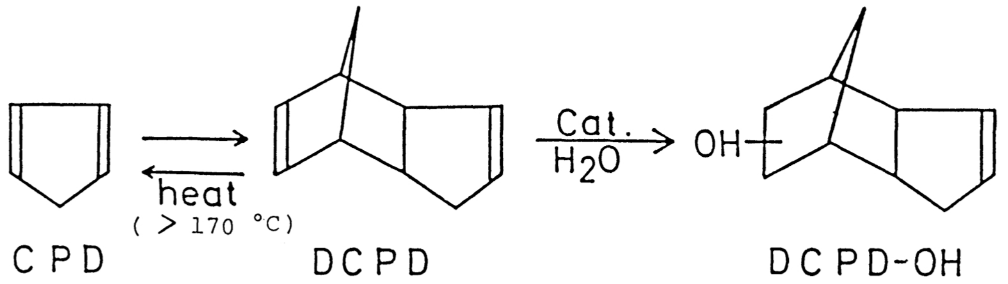

Table 1. Comparison of catalytic activities for DCPD hydration [a)]

Catalyst	Heat-treatment [b)] temperature/°C	Reaction temperature/°C	Conversion to hydrate/mol%
Amberlyst		100	2.0
Nafion H		150	0.3
Nafion H		170	0.4
SiO_2	400	170	2.0
TiO_2	400	170	5.2
Al_2O_3	400	170	3.1
SiO_2-Al_2O_3(N-631L)	500	170	4.0
TiO_2-SiO_2 [c)]	500	170	4.3
Niobic acid	300	170	17.0

a) The conversions were determined for the samples collected during the first thirty minutes of the run. W/F was kept constant at 5.9 $g \cdot h \cdot mol^{-1}$ except for the runs over Amberlyst(W/F=1.0 $g \cdot h \cdot mol^{-1}$) and Nafion H at 150 °C(W/F=3.2 $g \cdot h \cdot mol^{-1}$). b) The ion exchange resins were directly used without heat-treatment. c) The atomic ratio(Ti/Si) was 9.

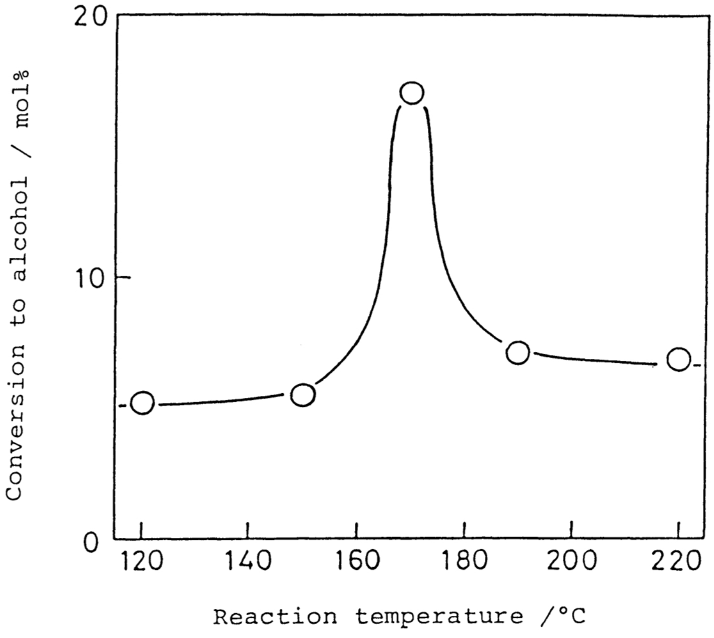

Fig.1. Effect of reaction temperature.
Heat-treatment temperature of niobic acid: 170 °C.

Figure 2 shows the effects of the heat-treatment temperature of niobic acid on its catalytic activity for the hydration. The decrease in the conversion to DCPD-OH at temperatures higher than 400 °C was ascribable to the decrease in the surface acidity of niobic acid. In fact, the conversion over niobic acid heat-treated at various temperatures was found to change in parallel with the change in catalyst acidity, which was determined by butylamine titration using benzenazodiphenylamine(pKa=1.5) as an indicator.

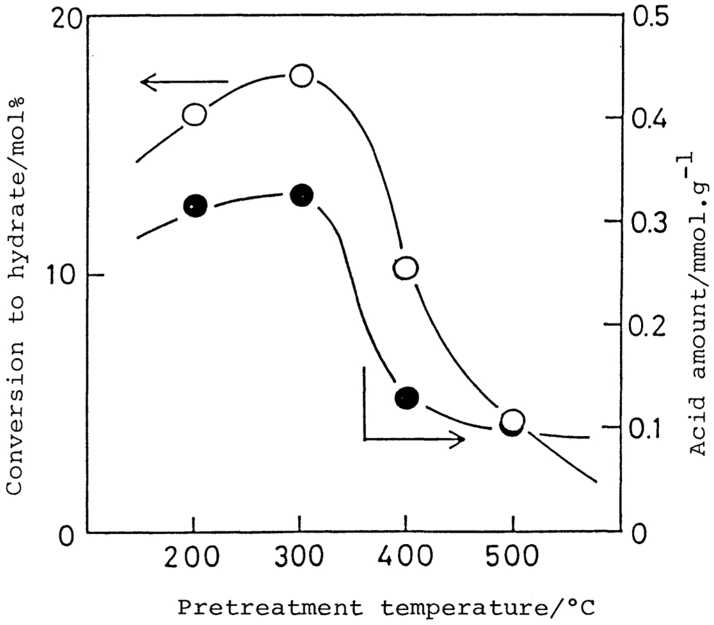

Fig.2. Effect of pretreatment temperature on catalytic activity and acid amount($H_o \le 1.5$).

References

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