Supplementary Information

Catalytic dehydration of fructose into 5-hydroxymethylfurfural by ion-exchange resin in mixed-aqueous system by microwave heating

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Detailed work-up procedure

Experiments by microwave heating were performed with the apparatus as shown in Fig. S1. The apparatus mainly consists of a multimode microwave generator with a K-type thermocouple, a stirring system, and a control box (Shikoku Keisoku μ Reactor, SMW-087, 2.45 GHz, maximum power 700 W), a reactor, a pressure gauge, a nitrogen cylinder, a cooling water tank and a vacuum pump. The reactor was composed of an inner thick-wall Pyrex glass tube (HPG-10, volume 10 ml, maximum supporting pressure 10 MPa, TaiatsuTechno. Corporation, Japan), an outer polycarbonate tube and two PEEK screw caps with special seal joint used to fix glass tube and PC tube (TaiatsuTechno. Corporation, Japan). The thermocouple was inserted into the reactor through a stainless steel sleeve and fixed with the inner wall of microwave oven to avoid microwave leakage from the oven and sparkle produced from the thermocouple. The leakage of microwave was monitored by a microwave survey meter (Holiday Industries Inc., Model HI-1501)) for safety. The temperature inside the reactor was controlled by the control box as being programmed.

A typical work-up procedure for the experiments was as follows. An solution (5 g) of fructose and a given amount of the catalyst were loaded into the glass tube. The glass tube was mounted into a PC tube that was closed with PEEK screw caps. This assembly was placed into the microwave oven as shown in Fig. S1. N₂ gas was used for purging air inside the reactor at a
pressure of about 1.2 MPa. Then the vacuum pump 14 was run to pump out the air out between
the inner glass tube and the outer PC tube to get a vacuum condition for insulation (reduced the
heat loss from glass tube to PC tube) and was good for the cooling water enter the PC tube
automatically to cool the reactor rapidly after reaction finished. When the microwave irradiation
was started, the reaction mixture could be heated up to 150 °C within 30 s. In the reaction
analyses, zero time was taken to be when the temperature reached 150 °C. After the desired
reaction time passed, the microwave irradiation was turned off, valve 9 was closed, the vacuum
pump 14 was stopped, and the valve 8 was opened to enter the cooling water from tank 20 into PC
tube automatically due to the pressure difference (the reaction solution was cooled down to below
60 °C within 60 s). After cooling, the valve 10 was opened and the N₂ gas inside the glass tube
was discharged. The reactor was taken down and the reaction solution was collected by washing
the glass tube with an amount of distilled water.

For the sand bath experiments, procedures for loading and recovering the samples were
basically the same as those used in the microwave heating experiments. Reactions were conducted
with SS 316 stainless steel tube bomb reactors (inner volume: 6 cm³). A given amount of solution
and resin were loaded into the reactor. Then N₂ gas was used for purging air inside the reactor by
pressurization to 1.2 MPa. After the sample was loaded, the reactor was submerged into a sand
bath and heated up to 150 °C within 60 s. Zero time was taken to be when the temperature reached
150 °C. Fig. S2 is a typical heating profile under microwave irradiation. After the reaction time
was reached, the reactor was taken out of the sand bath and quenched in a water bath that was at
room temperature. The samples in the reactor were collected by rinsing of the reactor with water.
The solid sample, namely resin was separated from the liquid sample by filtration before analysis.
Fig. S1. Microwave heating experimental setup
(1- Microwave oven, 2- Reaction solution and catalyst, 3- Polycarbonate outer tube, 4- Thick-walled glass reactor, 5- K-type thermocouple, 6- PEEK cap, 7, 8, 9, 10- Valve, 11- Pressure indicator, 12- Control box, 13- \( \text{N}_2 \) cylinder, 14- Vacuum pump, 15- Stirrer controller, 16- Stirrer, 17, 18- PEEK tube, 19- Observation window, 20- Cooling water tank,)
Fig. S2. A typical heating curve under microwave irradiation: 5 g fructose solution, 0.1 g resin, set temperature 150 °C, maximum power 700 W. T=Temperature, P=Power.