Supporting information

Hydrolysis–Dehydration of Cellulose: Efficiency of NbZr Catalysts under Batch and Flow Conditions

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Content

S1. List of chemicals used as HPLC standards

D-glucose $C_6H_{12}O_6$ (99%, Fisher Chemical), D-fructose $C_6H_{12}O_6$ (>99%, Sigma-Aldrich), D-mannose $C_6H_{12}O_6$ (>99%, Sigma-Aldrich), 5-Hydroxymethylfurfural $C_6H_6O_3$ (>98%, Acros Organics), maltose $C_{12}H_{22}O_{11}$ (> 90%, Acros Organics), levulinic acid $C_5H_8O_3$ (98%, Acros Organics), formic acid CH_2O_2 (Panreac), acetic acid $C_2H_4O_2$ (ReaChem), succinic acid $C_4H_6O_4$ (99%, Sigma-Aldrich), glycolic acid $C_2H_4O_3$ (99%, Sigma-Aldrich), glyceraldehyde (95%, Sigma-Aldrich), glycolaldehyde dimer (95%, Sigma-Aldrich) were used as HPLC standards.

S2. Characterization of Nb, Zr-catalysts

S2.1 Investigation of Nb, Zr-catalysts DR-UV-vis spectroscopy

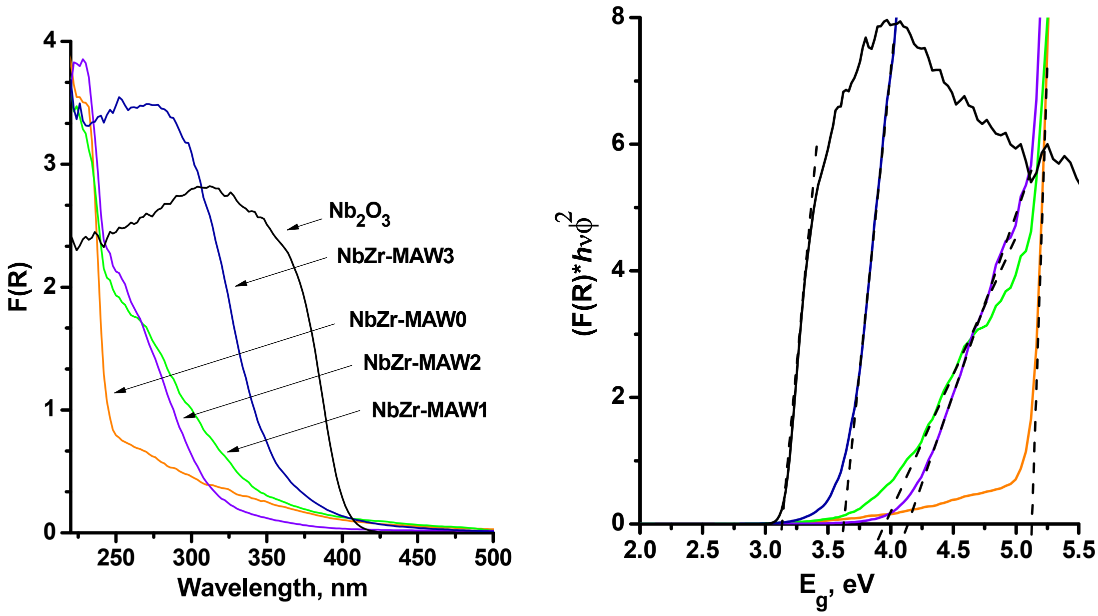

Figure S1. DR-UV-Vis spectra of NbZr-MAW samples and correlation between E_g. and:function$[F(R\infty)\ h\nu]^2$

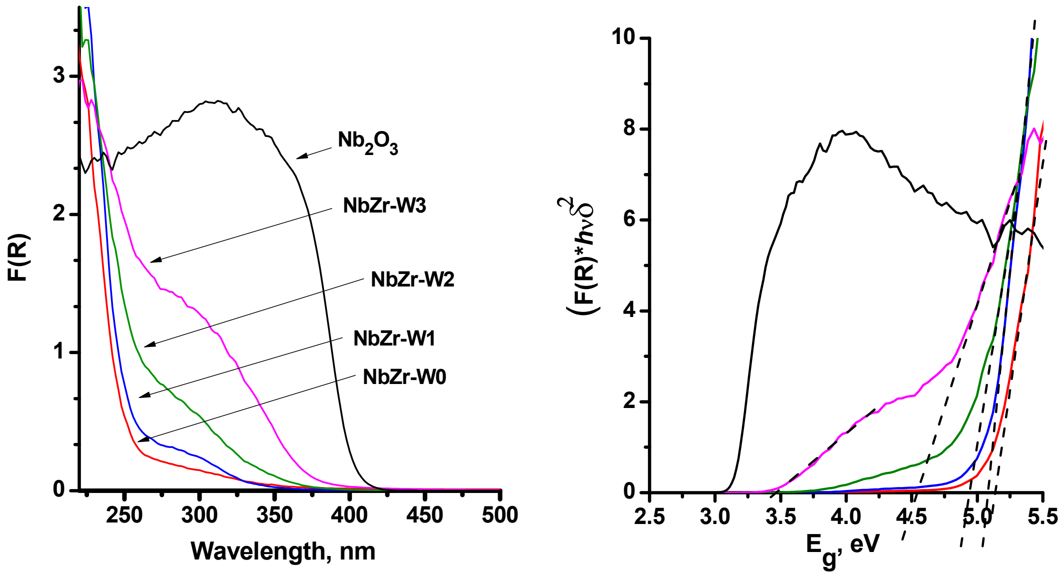

Figure S2. DR-UV-Vis spectra of NbZr-W samples and correlation between function $[F(R\infty)\ h\nu]^2$ and E_g.:

S2.2 Investigation of Nb,Zr-catalysts by DRIFT spectroscopy

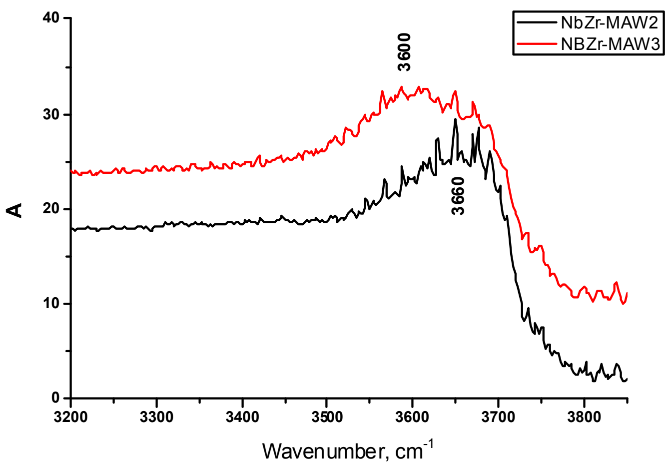

Figure S3. IR spectra of-MAW2 and NbZr-MAW3 samples calcination at 673 K.

S2.3 Investigation of acidic sites nature

Pyridine adsorption was used to determine the Brønsted (BAS) and Lewis (LAS) surface acid sites. After recording the IR spectrum of the dehydroxylated support, the sample was treated with pyridine vapor at room temperature. Then it was heated at 423 K for 15 minutes. Pyridine was downloaded for 30 minutes at 423 K to a residual vacuum of 2×10^{-2} Torr. Then the sample was cooled to room temperature and the IR spectrum was recorded. The concentration of BAS and LAS were estimated from the integrated intensity of the absorption band of the pyridinium ion with a maximum in the region of 1535 – 1550 cm^{-1} (A_0 – 3 cm μmol^{-1}) and 1445 cm^{-1} (A_0 – 3.5 cm μmol^{-1}).

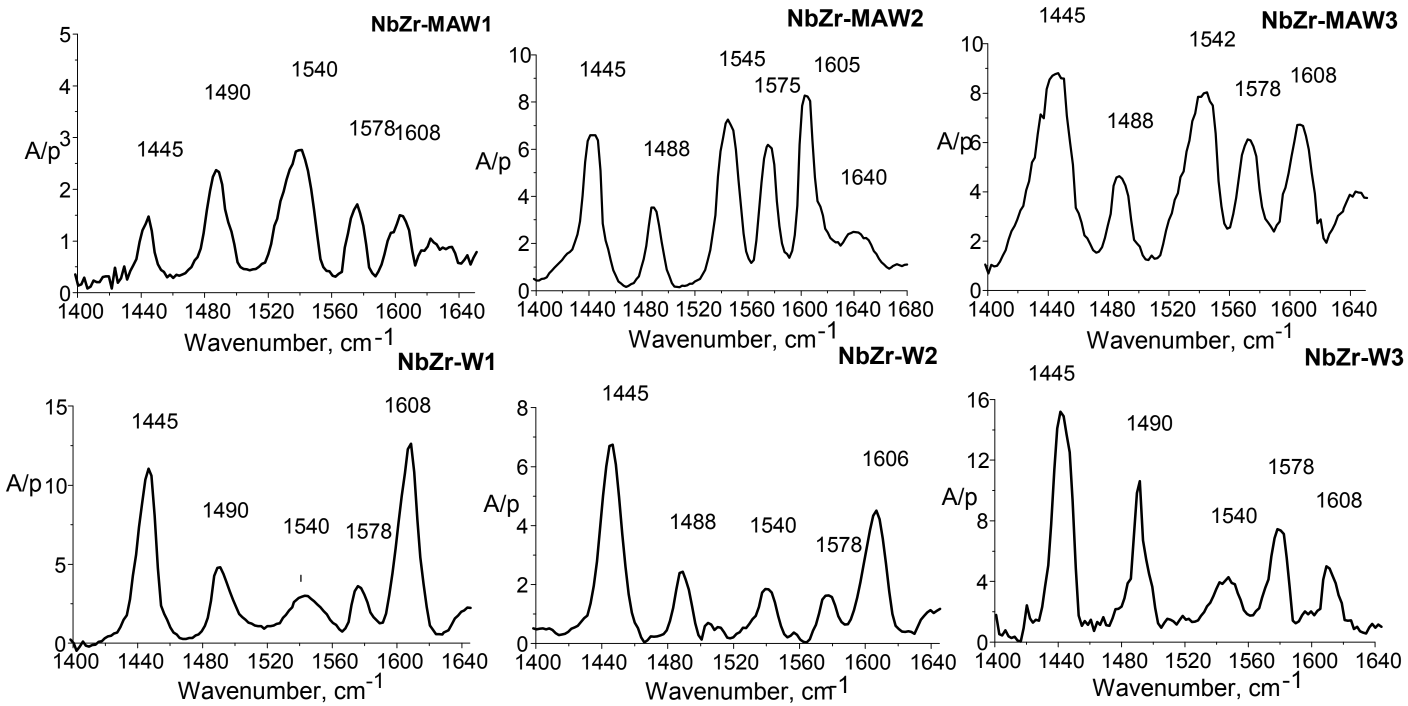

Figure S4. IR spectra of pyridine adsorbed on Nb,Zr-samples.

S3. Catalytic properties of Nb, Zr-catalysts

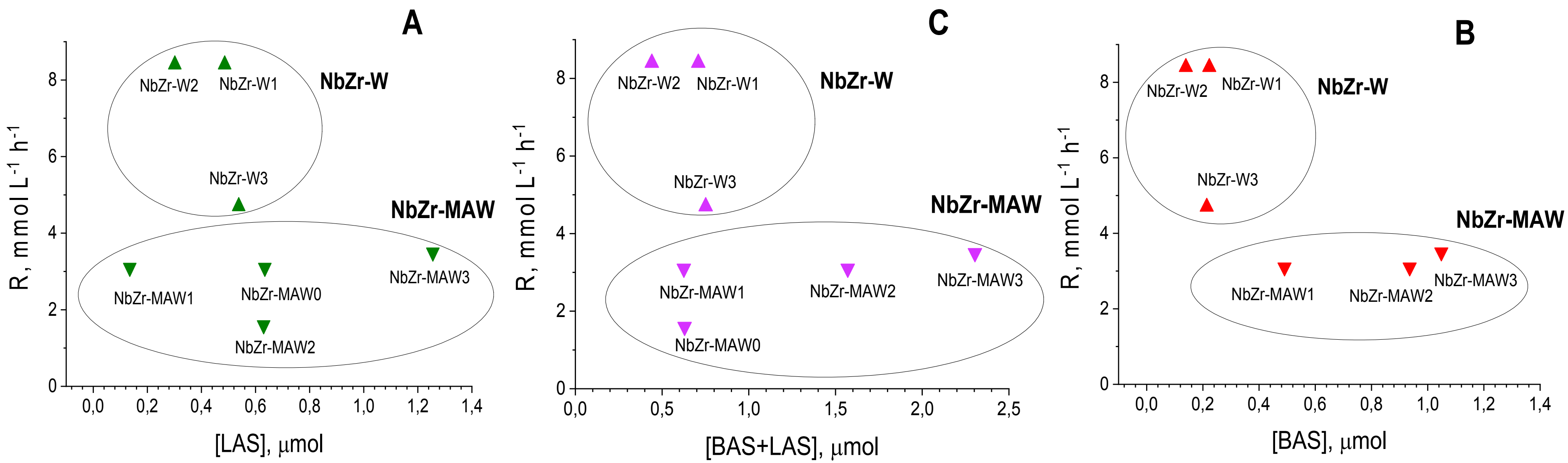

Figure S5. Dependence of the initial reaction rate on the amount of acid sites on the surface in the reaction of cellulose hydrolysis-dehydration. (Reaction conditions: 10 g L^{-1} of cellulose, 45 ml of water, 1 MPa of Ar, 453 K, 7 h. Concentration of catalyst: 1 g L^{-1} of NbZr-W and 0.5 g L^{-1} of NbZr-MAW)

S4. The scheme of the apparatus of hydrolysis-dehydration of cellulose under flow conditions

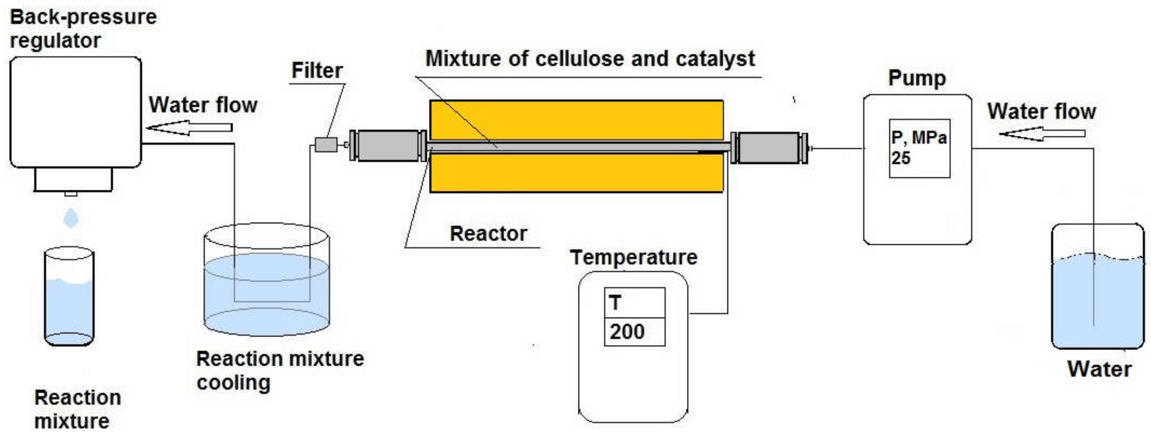

Figure S6. The scheme of the apparatus of hydrolysis-dehydration of cellulose under flow conditions