HYDROXYMETHYL FURFURAL OXIDATION METHODS

RELATED PATENT DATA

This patent resulted from a divisional of U.S. patent application Ser. No. 11/932,436 which was filed on Oct. 31, 2007 which claims priority under 35 U.S.C. §119 to U.S. Provisional Application No. 60/863,704, which was filed Oct. 31, 2006.

TECHNICAL FIELD

The invention pertains to hydroxymethylfurfural oxidation methods, methods of producing diformyl furan and methods of producing an oxidation catalyst.

BACKGROUND OF THE INVENTION

Hydroxymethylfurfural (HMF) is a compound which can be produced from various hexoses or hexose-comprising materials. HMF can in turn be converted into a variety of derivatives, many of which are currently or are quickly becoming commercially valuable. Oxidation of HMF can produce oxidation products including diformyl furan (DFF), hydroxymethyl furan carboxylic acid (HMFCA), formylfuran carboxylic acid (FFCA), and furandicarboxylic acid (FDCA). Uses for these oxidation products include but are not limited to adhesives, sealants, composites, coatings, binders, foams, curatives, monomers and resins.

Although numerous routes and reactions have been utilized for preparing one or more of the oxidation products set forth above, conventional methodology typically results in low HMF conversion, low product selectivity and/or low product yield. It is desirable to develop alternative methodologies for oxidation of HMF and production of HMF oxidation products.

SUMMARY OF THE INVENTION

In one aspect the invention pertains to a method of oxidizing hydroxymethylfurfural (HMF). The method includes providing a starting material which includes HMF in a solvent comprising water into a reactor. At least one of air and O_2 is provided into the reactor. The starting material is contacted with the catalyst comprising Pt on a support material where the contacting is conducted at a reactor temperature of from about 50° C. to about 200° C.

In one aspect the invention pertains to a method of producing diformylfuran. The method includes providing a mixture comprising HMF and an organic solvent. The mixture is contacted with a catalyst comprising active γ-MnO_2. The mixture is subjected to reflux temperature for a time of from about 6 hours to about 12 hours.

In one aspect the invention includes a method of producing an oxidation catalyst. ZrO_2 is provided and is calcined. The ZrO_2 is mixed with platinum (II) acetylacetonate to form a mixture. The mixture is subjected to rotary evaporation to form a product. The product is calcined and reduced under hydrogen to form an activated product. The activated product is passivated under a flow of 2% O_2.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

FIG. **1** shows conversion of HMF and selective production of furan dicarboxylic acid and formylfuran carboxylic acid as a function of time on stream utilizing a continuous flow reactor with a 5% platinum supported on carbon catalyst and a base set of parameters in accordance with one aspect of the invention. The parameters included P=150 psig, T=100° C., 0.828% Na_2CO_3 added to 1% HMF, liquid hourly space velocity (LHSV)=7.5-15 h^{-1}, air gas hourly space velocity (GHSV)=300 h^{-1}, catalyst reduced at 30° C. wet.

FIG. **2** shows HMF conversion and product selectivity as a function of time on stream using the catalyst of FIG. **1** at a decreased temperature (T=70° C.), LHSV=4.5-7.5 h^{-1} and air GHSV=300-600 h^{-1} (all other parameters and conditions being as set forth above with respect to FIG. **1**).

FIG. **3** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** and the parameters as set forth for FIG. **2** except for temperature (T=50° C.).

FIG. **4** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** and the conditions as set forth at FIG. **2** with the exception of the temperature which was T=30° C.

FIG. **5** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** and the conditions of FIG. **2** with a decreased concentration of Na_2CO_3 of 0.414% and T=100° C.

FIG. **6** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** and the conditions of FIG. **1** except with an increased Na_2CO_3 concentration of 1.66%.

FIG. **7** shows HMF conversion and product selectivity as a function of temperature using the catalyst of FIG. **1**. P=150 psig, 0.828% Na_2CO_3 added to 1% HMF, LHSV=7.5 h^{-1} air, GHSV=300 h^{-1}, data taken at time on stream=140 min.

FIG. **8** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at the specified temperature and GHSV (either air or O_2). P=150 psig, T=100-115° C., 2.486% Na_2CO_3 added to 3% HMF LHSV=4.5 h^{-1}, air GHSV=300-600 h^{-1} or O_2 GHSV=600 h^{-1}, catalyst reduced at 30° C. wet.

FIG. **9** shows HMF conversion and product selectivity as a function of time on steam utilizing the catalyst of FIG. **1** under air or O_2 at varied LHSV and/or GHSV. P=150 psig, T=130° C., 0.828% Na_2CO_3 added to 1% HMF, LHSV=7.5-15 h^{-1}, air GHSV=300-600 h^{-1} or O_2 GHSV=600 h^{-1}, catalyst reduced at 30° C. wet.

FIG. **10** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at P=150 psig air, T=100° C., 1% HMF, LHSV=7.5-15 h^{-1}, GHSV=300 h^{-1}.

FIG. **11** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** and the conditions of FIG. **10** with the exception of 0.8% added Na_2CO_3.

FIG. **12** shows conversion of HMF and selective production of the indicated products as a function of time on stream utilizing a continuous flow reactor with a 5% Pt supported on SiO_2 catalyst and a base set of parameters in accordance with one aspect of the invention; 1% HMF, 150 psig air, 60-100° C., LHSV=13-19.6 h^{-1}, GHSV=261 h^{-1}.

FIG. **13** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **12** in the presence of 0.8% Na_2CO_3. (1% HMF, 0.8% Na_2CO_3, 150 psig air, 100° C., LHSV=13-6.5 h^{-1}, GHSV=261 h^{-1}.)

FIG. **14** shows HMF conversion and product selectivity utilizing a 9.65% Pt supported on carbon catalyst. The conditions utilized were P=150 psig, T=100° C., 0.828%