



Hydrogenation of 2,5-dimethylfuran on hexagonal-boron nitride- and silica-supported platinum catalysts

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ABSTRACT

Hydrogenation of furanic compounds is one of the important reactions for upgrading of bio-oils and production of diesel fuels. Platinum catalysts supported on amorphous silica and hexagonal boron nitride (h-BN) were prepared by incipient wetness impregnation and subsequent reduction, and were used for the vapor-phase hydrogenation of 2,5-dimethylfuran in hydrogen at atmospheric pressure and a temperature range of 150–350 °C. For the same amount of Pt loading (1 wt%), the particle size of Pt supported on h-BN was larger than that on silica, resulting in a lower amount of CO chemisorption for Pt/BN than that for Pt/SiO₂. Using the same amount of active sites, Pt/BN exhibited a 3-fold higher turnover frequency than Pt/SiO₂ for the hydrogenation of 2,5-dimethylfuran whereas both catalysts gave similar product distributions with high selectivity to 2-hexanone at any conversion and low selectivity to *n*-hexane at high conversion. Contact time studies of 2,5-dimethylfuran hydrogenation on Pt/BN suggested that 2,5-dimethylfuran formed the ring-opening product, 2-hexanone and the ring-saturation product, 2,5-dimethyltetrahydrofuran in parallel, with the rate of the direct furan ring-opening being 9-fold higher than that of the furan ring-saturation.

1. Introduction

The transformation of lignocellulosic biomass into fuels and chemicals has attracted much attention as an alternative to fossil fuels [1]. Furanic compounds such as 5-methylfurfural, 5-hydroxymethylfurfural, 2-methylfuran, 2,5-dimethylfuran (2,5-DMF) are representative of biomass derivatives which are contained in fast pyrolysis oil (bio-oil) [2] and are also obtained from (hemi)cellulose by catalytic conversion via multi-steps including hydrolysis, dehydration and hydrogenation [3]. Hydrogenation and hydrogenolysis of furan ring compounds are of importance for upgrading of bio-oil [4] as well as production of diesel including jet fuels [5,6] and chemical intermediates. It is known that these reactions are catalyzed over the Adams platinum catalyst [7] and carbon-supported metals such as Pt [5,8–12], Pd [8,9,12], Ru [8,9,13], Ir [8], Rh [9], Ni [8] and Co [8], and other catalysts such as carbides [14] or phosphides [15,16]. Among carbon-supported metal catalysts, the Pt catalyst was the most active for 2,5-DMF hydrogenation [8,9]. Products with Pt were 2,5-dimethyltetrahydrofuran (2,5-DMTHF), 2-hexanol, 2-hexanone and *n*-hexane, however the product selectivities were much different from those of other metals. The Pt catalyst selectively afforded ring-opened products such as 2-hexanol at low temperature and 2-hexanone at high temperature whereas the other metal catalysts selectively gave the ring-saturated product, 2,5-DMTHF. In

contrast to the extensive studies on the effect of metal species on the activity, those of supports and particles sizes of Pt catalysts are limited. One study reported that Pt catalysts with similar particle sizes, 4–5 nm, loaded on three supports, Pt/C, Pt/Al₂O₃, Pt/NbOPO₄, showed almost the same turnover frequencies for hydrogenation of 2,5-DMF at low temperature (80 °C) in the liquid-phase whereas they showed different activities for hydrogenation of 2-hexanone owing to different Lewis acidity of the supports [9]. Another investigation showed that a Pt catalyst with a small average particle size of 0.97 nm, prepared by the atomic layer deposition method on alumina, 0.47 wt% Pt/Al₂O₃ exhibited much higher selectivity to *n*-hexane than a commercial 5 wt% Pt/C when the reactivity was tested using the same gas hourly space velocity (GHSV) of 2500 h^{−1} and under full conversion of 2,5-DMF at all reaction temperatures within the range 80–300 °C for all catalysts tested [10]. However, that study did not use the same amount of surface metal sites loaded in the reactor, and the full conversion indicated mass transfer limitations. Therefore, it is helpful to investigate the activity of Pt catalysts with small particle sizes loaded on supports other than those studied previously for 2,5-DMF hydrogenation using the same number of active sites of the catalysts in the absence of mass-transfer limitation. Here 1 wt% Pt catalysts supported on two different supports were prepared and tested for the vapor-phase 2,5-DMF hydrogenation under 1 atm of hydrogen. Amorphous silica and hexagonal-boron

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nitride (h-BN) were chosen as supports because silica is widely known as an inert support and h-BN is also recognized as inert but recently was found to be active itself for hydrogenation of alkenes [17].

2. Experimental

2.1. Materials

The chemicals hexachloroplatinic acid (H_2PtCl_6 , > 99.9%, Sigma-Aldrich), boron nitride (Wako) and SiO_2 (CAB-O-SIL EH-5, Cabot) were used as received. The chemicals as reactants were 2,5-dimethylfuran (2,5-DMF, 99.88%, Apollo Scientific), 2,5-dimethyltetrahydrofuran (2,5-DMTHF, > 98%, TCI) and toluene (> 99.5%, Wako).

2.2. Catalyst preparation

The supported platinum catalysts were prepared by incipient wetness impregnation and subsequent reduction. A quantity of 1 wt% of hexachloroplatinic acid dissolved in distilled water was impregnated drop-wise to the incipient wetness point on supports (boron nitride and SiO_2) which were dried beforehand at 100 °C overnight. Quantities of 1 g of the precursor-support mixtures were dried at 100 °C for 24 h and reduced under a hydrogen flow of 50 mL min^{-1} at 350 °C for 1 h with a heating rate of 5 °C min^{-1} before the measurements. The commercial boron nitride was ball-milled at 400 rpm for 12 h using a planetary ball mill (Pulverisette 7, Fritsch, zirconia balls (10 mm diameter)) to make the support.

2.3. Catalyst characterization

The crystal structure of the catalysts was determined by X-ray diffraction (XRD, RINT-2700, Rigaku) with Cu K α radiation ($\lambda = 0.1548$ nm) at a voltage of 40 kV and a current of 100 mA. Scans were obtained at a speed of 2° min^{-1} with step width of 0.02° for 2 θ values from 20° to 60°. The surface area of the catalysts was measured by nitrogen adsorption (BELSORP-mini II, Microtrac-BEL) using the Brunauer-Emmett-Teller (BET) method. Prior to the measurement, samples were evacuated at 200 °C for 2 h. The amount of active sites on the catalysts was estimated by carbon monoxide (CO) chemisorption. Quantities of 0.5 g of samples were placed in a quartz reactor and were reduced in hydrogen flow at 350 °C for 1 h and then cooled to 50 °C in helium flow. Pulses of 3% CO/He were introduced over the pretreated catalysts for 21 cycles at 50 °C. The diminished peak areas of the mass spectrometer signal at $m/z = 28$ were used to calculate the amount of adsorbed CO. About 10% experimental errors should be considered because the measurement using mass spectrometer involved some short intervals for detection of CO signals.

The particle size distribution of supported Pt nanoparticles was evaluated by transmission electron microscopy (TEM) (Hitachi H-7650) at 100 kV. A carbon-coated copper grid was used as a substrate and the catalyst was dispersed in water and put on the grid.

The local structure of supported Pt nanoparticles was estimated by X-ray absorption fine structure (XAFS) spectroscopy at beamline BL-9C of the Photon Factory of the Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK) in Japan. The synchrotron ring operated at 2.5 GeV and 430 mA. About 80 mg of sample was pressed into a pellet 10 mm in diameter, and set in the center of an in situ XAFS cell. Hydrogen was introduced at a flow rate of 50 mL(NTP) min^{-1} and the cell was heated from room temperature to 350 °C at a rate of 10 °C min^{-1} and then kept at 350 °C for 1 h. After in situ reduction, the measurements were performed at 350 °C under hydrogen flow in transmission mode. The collected data were analyzed by the software program REX 2000 (Rigaku Co.). The parameters for the curve fitting analysis were obtained with FEFF. The curve-fitting was conducted in the range of $k = 0.25$ –1.4 nm^{-1} .

The adsorption behavior of 2,5-dimethylfuran on Pt/BN and Pt/ SiO_2

was examined by Fourier transform infrared (FTIR) spectroscopy. About 20 mg of samples was pressed into a disk with 20 mm diameter, and set in the center of a cell. The cell was heated from room temperature to 350 °C at a rate of 10 °C min^{-1} in vacuum and then kept at this temperature for 1 h in vacuum (below 0.003 Torr). After the cell was cooled to 50 °C, 2,5-dimethylfuran (ca. 5 Torr) was introduced to the cell. After 30 min, the cell was evacuated at 50 °C for 30 min and heated to 300 °C in vacuum. The IR spectra were recorded by using the spectrometer (Jasco FT/IR-6100) equipped with mercury cadmium telluride (MCT) detector at 4 cm^{-1} resolution.

The solid acid property was examined by temperature-programmed desorption of ammonia (NH_3 -TPD)(TPD-1-AT, Microtrac BEL). Quantities of 20 mg of sample were heated from room temperature to 350 °C in He (50 $\text{cm}^3 \text{min}^{-1}$) at a rate of 10 min^{-1} and kept at this temperature for 1 h. After the samples was cooled to 100 °C and held at this temperature for 30 min, a 10% NH_3 /He stream (50 $\text{cm}^3 \text{min}^{-1}$) was introduced for 0.5 h. The saturated sample was flushed with He (50 $\text{cm}^3 \text{min}^{-1}$) for 30 min, and then the temperature was increased from 100 to 600 °C at a heating rate of 10 °C min^{-1} . Masses 16 and 17 were monitored during the desorption by a mass spectrometer. As a comparison, H-ZSM5 (Si/Al = 15) zeolite with 1.0 mmol g^{-1} of acid sites was used.

2.4. Hydrogenation of 2,5-Dimethylfuran

The activity tests of hydrogenation of 2,5-dimethylfuran (2,5-DMF) were carried out in a fixed-bed flow reactor in the gas phase at ambient pressure and a temperature range of 150–350 °C. Amounts of catalysts equivalent to 0.87 μmol of active sites as determined by CO chemisorption were used. Before the activity testing, the catalysts were pretreated in the reactor in hydrogen flow (200 $\text{cm}^3(\text{NTP}) \text{min}^{-1}$) at 350 °C for 1 h. The inlet concentration of 2,5-DMF was 10 mol% in a flow of hydrogen of 50 $\text{cm}^3(\text{NTP}) \text{min}^{-1}$ (34 $\mu\text{mol s}^{-1}$). The reactant also contained 5 vol% of toluene as an internal standard and was delivered through a bubbler maintained at 35 °C to obtain a ratio of H_2 /2,5-DMF of 10/1. In the experiments, the contact time was kept constant at 0.26 s. Contact time is defined as follows.

$$\text{Contact time [s]} = \frac{\text{CO uptake} [\mu\text{mol/g}] \times \text{Catalyst weight [g]}}{\text{Reactant molar flow rate} [\mu\text{mol/s}]}$$

After introduction of the reactant the temperature was varied in the following order, 350 °C \rightarrow 250 °C \rightarrow 150 °C \rightarrow 200 °C \rightarrow 300 °C. Product gas mixtures were analyzed using an on-line gas chromatograph (GC; GC-2014, Shimadzu) equipped with a flame ionization detector (FID) and a commercial HP-1 capillary column. The contact time study was carried out in the same manner, except at a fixed temperature of 175 °C and various contact times from 0.06 to 0.43 s. The contact time was controlled by changing the hydrogen flow rate from 25 to 190 $\text{cm}^3(\text{NTP}) \text{min}^{-1}$ using the same amount of the catalyst. GC-FID and GC-MS analysis confirmed that toluene was not hydrogenated under the reaction conditions. The equilibrium constant for toluene hydrogenation is reported as $K_{eq} = 3.60 \times 10^9 \text{ kPa}^3 \times e^{-26179 \left(\frac{1}{T} - \frac{1}{650} \right)}$ [18]. Under the reaction conditions in this study, the equilibrium conversion of toluene is negligible (< 0.1%) at a higher temperature than 200 °C. Although the equilibrium conversion of toluene is 98% at 150 °C, no formation of methylcyclohexane was observed in this experiment. This is probably due to low activity of platinum for the hydrogenation and competitive adsorption of 2,5-dimethylfuran.

3. Results and discussion

Fig. 1 shows XRD patterns of 1 wt% Pt/BN, 1 wt% Pt/ SiO_2 and their supports. The Pt/BN catalyst showed four peaks at 26.6°, 41.6°, 39.5° and 46.4°. The former two peaks are derived from h-BN support, corresponding to the (002) interlayer reflection and the (100) in-plane

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