Catalysis Today 269 (2016) 122–131

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic conversion of sorbitol to gasoline-ranged products without external hydrogen over Pt-modified Ir-ReO_x/SiO_2

Sibao Liu [a], Yasuyo Okuyama [b], Masazumi Tamura [a], Yoshinao Nakagawa [a,*],
Akio Imai [b], Keiichi Tomishige [a,*]

[a] *Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan*
[b] *Central Research & Development Laboratory, Showa Shell Sekiyu K.K., 4052-2 Nakatsu, Aikawa-cho, Aikoh-gun, Kanagawa-ken, Japan*

ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form 3 October 2015
Accepted 8 October 2015
Available online 11 November 2015

Keywords:
Sorbitol
Gasoline
Aqueous phase reforming
Hydrogenolysis

ABSTRACT

Deoxygenation of sorbitol was carried out over a Pt-modified Ir-ReO_x/SiO_2 catalyst in biphasic solvent system (*n*-decane + H_2O) without external hydrogen. Good yield of gasoline-ranged products was obtained including C5–C6 alkanes and C2–C6 mono-functionalized compounds such as ketones, alcohols, cyclic ethers and carboxylic acids. The Pt(3 wt%)-Ir-ReO_x/SiO_2 catalyst showed the best performance in the production of gasoline-ranged products. The maximum yield of gasoline-ranged products was 42%. The distribution of the products can be tuned by the addition of HZSM-5. The main products were C5–C6 alkanes with addition of HZSM-5 while the main products were C2–C6 mono-functionalized compounds without addition of HZSM-5. Characterizations such as TPR, XRD, TEM, XANES, EXAFS, CO adsorption were performed. The results demonstrated that the Pt-Ir-ReO_x/SiO_2 catalyst showed the structure of Pt-Ir alloy particles partially covered with ReO_x species. The number of surface Pt atoms in Pt(3)-Ir-ReO_x/SiO_2 was larger than that of Pt/SiO_2 or Pt-ReO_x/SiO_2 because of the small size of Pt-Ir alloy particles. The large number of surface Pt atoms and the synergetic effect of Pt, Ir and ReO_x species make the catalyst efficiently generate hydrogen by aqueous phase reforming of sorbitol, and the generated hydrogen is consumed in the hydrogenolysis C—O bonds.

1. Introduction

Decreasing oil supplies, increasing energy demand and global warming issues provide incentives to conversion of renewable biomass into high-quality transportation fuels and valuable chemical feedstocks [1–9]. Recently, particular interest has been attracted on producing gasoline-ranged products by aqueous-phase hydrodeoxygenation of biomass-derived sugars or sugar alcohols, especially sorbitol [10–20]. Several Pt-based catalysts supported on carbon, solid acids, metal oxide and metal oxide phosphates has been reported in the literature as promising catalysts for this process [10–20]. The total yield of gasoline-range products including C5–C6 alkanes and C2–C6 mono-functionalized compounds could reach around 40–70% over these Pt-based catalysts. However, a high pressure of hydrogen was needed for the processes. Considering the high cost of fossil-derived hydrogen and potential safety issues which caused by the high pressure hydrogen, the industrial prospect of this process is becoming a challenge. In 2002, Dumesic et al. reported aqueous phase reforming (APR) of polyols (sorbitol, glycerol and ethylene glycol) to produce hydrogen over Pt-based catalyst at 498 K [21]. Later the same group [22] and the group of Murzin et al. investigated APR of sorbitol and found that some amounts of less-oxygenated organic products such as ≥C4 mono-oxygenates can be formed [23,24]. It seems worthwhile to evaluate the possibility of production of useful less-oxygenated organics using in situ generated hydrogen and catalysts with higher hydrogenolysis activity. A lot of works on the conversion of glycerol to 1,2-propanediol by using this biorefinery concept were reported [25–33]. However, the most abundant sugar alcohol, sorbitol, has unexpectedly attracted very little attention [10,21–24,34]. Sorbitol is a very important biomass-derived platform molecule, which can be produced from cellulose by hydrolysis and hydrogenation [35–37]. Therefore, efficient conversion of sorbitol to gasoline-ranged products in high yield without external hydrogen could be very meaningful.

In our previous work, we have found that Ir-ReO_x/SiO_2 catalyst shows high C—O hydrogenolysis activity and almost no C—C cracking activity [38,39]. However, APR of polyols involves C—C dissociation and thus the catalyst should have some C—C

---

* Corresponding authors.
E-mail addresses: yoshinao@erec.che.tohoku.ac.jp (Y. Nakagawa), tomi@erec.che.tohoku.ac.jp (K. Tomishige).

http://dx.doi.org/10.1016/j.cattod.2015.10.023
0920-5861/

cracking activity. Therefore, in this study, we modified Ir-ReO$_x$/SiO$_2$ with other noble metals, especially Pt, to improve its C—C cracking activity and balance the C—O and C—C dissociation performance to obtain high yield of gasoline-ranged products from sorbitol.

2. Experimental

2.1. Catalyst preparation

The SiO$_2$ (G-6, BET surface area 535 m^2/g) supplied by Fuji Silysia Chemical Ltd. was used as a support of the catalysts. Before impregnation, SiO$_2$ was calcined in air at 973 K for 1 h. Ir-ReO$_x$/SiO$_2$ catalysts were prepared by sequential impregnation method as described previously [40–48]. First, Ir/SiO$_2$ was prepared by impregnating with an aqueous solution of H$_2$IrCl$_6$ (Furuya Metals Co., Ltd). After evaporating the solvent at ≤353 K and drying at 383 K for 12 h, they were impregnated with an aqueous solution of NH$_4$ReO$_4$ (Soekawa Chemical Co., Ltd.). These catalysts were calcined in a crucible in air at 773 K for 3 h after drying at 383 K for 12 h. Then the obtained Ir-ReO$_x$/SiO$_2$ catalyst was impregnated with an aqueous solution of H$_2$PtCl$_6$ (Soekawa Chemical Co., Ltd.), RhCl$_3$ (Wako Pure Chemical Industries, Ltd.), PdCl$_2$ (Soekawa Chemical Co., Ltd.), or RuCl$_3$ (Strem Chemicals Co., Ltd.). After evaporating the solvent and drying at 383 K for 12 h, they were calcined in air at 773 K for 3 h. The loading amounts of Ir and Re were 4.0 and 7.8 wt%, respectively (Re/Ir molar ratio = 2), and that of additive was represented by the weight percent of the additives to the total catalyst in parenthesis like M(x)-Ir-ReO$_x$/SiO$_2$ (M = Pt, Rh, Pd, Ru). All the catalysts were used in powdered form with a granule size of <100 mesh. HZSM-5 [JRC-Z5-90 H(1), Süd-Chemie Catalysts and Catalysis Society of Japan, Si/Al$_2$ = 90] was used as received.

2.2. Activity tests

Activity tests were performed in a 190-ml stainless steel autoclave with an inserted glass vessel. The catalyst was put into an autoclave together with a spinner and an appropriate amount of water and heated at 473 K with 8 MPa H$_2$ for 1 h for the reduction pretreatment. The stirring rate was 250 rpm. After the pretreatment, the autoclave was cooled down, and hydrogen was removed. Sorbitol (0.5 g, Wako Pure Chemical Industries, Ltd., 98%) and *n*-decane (20 ml; Tokyo Chemical Industry Co. Ltd., 99%) were put into the autoclave. HZSM-5 was also added when necessary. After sealing the reactor, the air content was purged by flushing three times with Ar (1 MPa, 99.99%; Nippon Peroxide Co., Ltd.). The reactor was pressurized with Ar to 0.5–4.0 MPa at room temperature and then heated to set temperatures (443–473 K). The heating took about 1–1.5 h. After the temperature reached the set one, the temperature was kept for appropriate reaction time. The stirring rate was 500 rpm. After reaction, the reactor was cooled down by using ice bath and the gases were collected in a gas bag. The reaction mixture was separated into organic and aqueous phases. The autoclave contents were transferred to a vial, and the catalyst was separated by centrifugation and filtration.

The products were isosorbide, ketones: 2-hexanone, 3-hexanone, 2-pentanone, 3-pentanone, butanone and actone; mono-alcohols: 1-hexanol, 2-hexanol, 3-hexanol, 1-pentanol, 2-pentanol and 3-pentanol; cyclic ethers: 2-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran; acids: acetic acid, propanoic acid, butanoic acid, valeric acid and hexanoic acid; alkanes: *n*-hexane, 2-methylpentane, 3-methylpentane, *n*-pentane, *n*-butane, propane, ethane and methane; CO$_2$; H$_2$ and other products that could not be identified. Sorbitol and isosorbide in the aqueous phase were analyzed by using HPLC (Shimadzu LC-10A) with a refractive index detector (RID) and a Phenomenex Rezex RPM-Monosaccharide Pb + 2 column (diameter 7.8 mm, 300 mm). Ketones, mono-alcohols and acids in the aqueous phase were analyzed by using gas chromatograph (Shimadzu GC-2014) equipped with TC-WAX capillary column (diameter 0.25 mm, 30 m) and FID. Alkanes, ketones, cyclic ethers and mono-alcohols in the organic phase were analyzed by gas chromatograph (Shimadzu GC-2014) equipped with DB-1 capillary column (diameter 0.25 mm, 30 m) and FID. Alkanes in the gas phase were analyzed by gas chromatograph (Shimadzu GC-2014) equipped with an Rtx-1-PONA capillary column (diameter 0.25 mm, 100 m) and FID. CO$_2$ in the gas phase was analyzed by gas chromatograph (Shimadzu GC-2014) equipped with a Gaskuropack 54 column, a methanator and FID, and H$_2$ was analyzed by the same GC with MS-13X packed column and TCD.

The conversion of substrate (sorbitol) and the yield of products were calculated on the carbon basis and defined as follows:

$$\text{Conversion [\%C]} = \frac{\text{mol of total C atoms in substrate} - \text{mol of C atoms in unreacted substrate}}{\text{mol of total C atoms in substrate}} \times 100$$

$$\text{Yield of detected products [\%C]} = \frac{\text{mol}_{\text{product}} \times \text{C atoms in product}}{\text{mol of total C atoms in substrate}} \times 100$$

$$\text{Loss of carbon balance [\%C]} = \text{Conversion} \times 100 - \text{the sum of yield of detected products} \times 100$$

The conversion of sorbitol with hydrogen was also conducted with the same method. The pressure of hydrogen was 6 MPa at room temperature. In the case of conversion of glycerol (Wako Pure Chemical Industries, Ltd., >99%), organic solvent (*n*-decane) was not used.

The used catalyst was washed with excess water, dried in air and then calcined at 773 K for 3 h. A slight loss (<15% in weight) was observed during the recovery process and was compensated with fresh catalyst in each reuse experiment. Before the activity test, the reduction pretreatment are carried out again in the same way as for the fresh catalyst. The amount of eluted metal during the reaction was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Scientific iCAP 6500).

2.3. Catalyst characterization

Temperature-programmed reduction (TPR) was carried out in a fixed-bed reactor equipped with a thermal conductivity detector using 5% H$_2$ diluted with Ar (30 ml/min). The amount of catalyst was 0.05 g, and the temperature was increased from room temperature to 1123 K at a heating rate of 10 K/min.

X-ray diffraction (XRD) patterns were recorded by a diffractometer (Rigaku MiniFlex 600). Average metal particle size was estimated by using the Scherrer equation [49].

The X-ray absorption near-edge structure (XANES) spectra were measured at the BL01B1 station at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2015A1134). The storage ring was operated at 8 GeV, and a Si (1 1 1) single crystal was used to obtain a monochromatic X-ray beam. Two ion chambers for I_0 and I were filled with 85% N$_2$ + 15% Ar and 50% N$_2$ + 50% Ar, respectively, for Pt L_3-edge, Re L_3-edge and Ir L_3-edge measurements. We prepared the sample after the catalytic use as follows. The catalytic reaction was carried out in an autoclave. The reaction conditions were the same as in activity tests. After cooling, the wet catalyst powder was transferred to the measurement cell in