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Selective transformation of hemicellulose (xylan) into *n*-pentane, pentanols or xylitol over rhenium-modified iridium catalyst combined with acids

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Abstract

n-Pentane, pentanols and xylitol can be separately produced from hemicellulose (xylan) over Ir-ReO_x/SiO_2 catalyst combined with acids by simply adjusting the reaction conditions. *n*-Pentane can be produced by using Ir-ReO_x/SiO_2 combined with HZSM-5 + H_2SO_4 in biphasic solvent system (4 ml *n*-dodecane + 9.5 ml H_2O) with reaction temperature 463 K for 24 h. Pentanols can be produced by using Ir-ReO_x/SiO_2 combined with H_2SO_4 in biphasic solvent system (20 ml *n*-dodecane + 9.5 ml H_2O) with reaction temperature 413 K for 144 h. Xylitol can be produced by using Ir-ReO_x/SiO_2 combined with H_2SO_4 in aqueous phase with reaction temperature 413 K for 12 h. The highest yields of *n*-pentane, pentanols and xylitol could reach 70%, 32% and 79%, respectively. The reuse of the catalyst was feasible when the catalyst was regenerated by calcination at 773 K for 3 h. The calcination step is for removing the humins which were formed at the hydrolysis + hydrogenation step during conversion of xylan. The humins covered the active site of Ir-ReO_x/SiO_2 and HZSM-5, and they deactivated Ir-ReO_x/SiO_2 in C-O hydrogenolysis performance in part. The mineral ions (such as Na^+ and K^+) in xylan decreased the hydrogenolysis activity of Ir-ReO_x/SiO_2 significantly since the mineral ions can make the number of hydroxorhenium site (Re-OH) smaller, which is the active site of Ir-ReO_x/SiO_2 for C-O hydrogenolysis, by ion exchange. The appropriate amount of H_2SO_4 addition is very crucial for production of target products in high yield. The addition of H_2SO_4 not only neutralized the residual alkali of xylan after being isolated from lignocellulose to make the reaction solution acidic, but also improved the C-O hydrogenolysis activity of Ir-ReO_x/SiO_2 through increasing the number of hydroxorhenium site by competitive adsorption on Re site with mineral ions.

Keywords

hemicellulose, hydrogenolysis, *n*-pentane, pentanol, xylitol

1. Introduction

Biomass and its derived substrates are playing a more and more important role in replacing non-renewable fossil resources in the production of transportation fuels and chemical products because of dwindling fossil resources and global warming.[1-10] Lignocellulose is the most abundant biomass resource, which comprises three different fractions: cellulose (40-50%), hemicellulose (20-30%), and lignin (20-30%). All of these fractions have high oxygen content, and the conversions to useful chemicals and fuels usually require reduction. Recently, numerous researches focused on reductive conversion of cellulose[11-14] and lignin[15-19]. On the other hand, the transformation of hemicellulose, which is mainly composed of pentoses (xylose and arabinose), usually starts with hydrolysis to pentose[20-23] or further dehydration to furfural[24-26].

One-pot conversion of hemicellulose to chemicals by reduction is less extensively studied[27-31]. Conversion of xylan, which is a kind of hemicellulose abundant in hardwood, into xylitol was reported with the yield of 50-80% by using Ru/C[27-28] or Pt-SnO_x/Al_2O_3[29]. Xylitol can be served as an artificial sweetener in food. While selective productions of long chain hydrocarbons[6, 32-36], 2-methylfuran[37-38], furan[38], tetrahydrofuran derivatives[39-41], cyclopentane derivatives[42-43], pentanediols[44-47] from furfural have been extensively reported[37-38, 44-47], there are few reports on production of *n*-pentane and pentanols from furfural[48-49]. In addition, a small number of researches on conversion of xylitol to *n*-pentane and pentanols by hydrogenolysis have been reported[50-54]. On the other hand, both *n*-pentane and pentanols can be used as organic solvents and as components of gasoline or fuel additives.[55] However, production of *n*-pentane or pentanols from furfural or xylitol needs the extra steps of hydrolysis + dehydration or hydrolysis + hydrogenation of xylan. Therefore, one-pot reductive transformation of xylan to xylitol, pentanols and *n*-pentane with a heterogeneous catalyst is more attractive and meaningful.

Both of the xylan and cellulose are polysaccharides. One-pot catalytic conversion of cellulose to sorbitol[11-14, 56-60], hexanols[61] and hexanes[62-64] by hydrolysis + hydrogenation or hydrogenolysis methods has been numerously reported, especially conversion to sorbitol. Sels et al.[63] and Ma et al.[64] reported catalytic systems for conversion of cellulose to *n*-hexane using Ru/C and acid catalysts. In these systems, cyclic intermediates such as 5-hydroxymethylfurfrual (HMF) and cyclic ethers were involved. On the other hand, we have very recently found that Ir-ReO$_x$/SiO$_2$ catalyst combined with HZSM-5 was effective in production of *n*-hexane from cellulose (~80% yield)[62] and Ir-ReO$_x$/SiO$_2$ catalyst combined with H_2SO_4 was effective in production of hexanols from mechanocatalytic depolymerized cellulose (~60% yield)[61]. The reaction for production of hexanes dominantly proceeds via hydrogenolysis of sorbitol step by step, and cyclic ethers are hardly formed. Therefore, in this work, we used Ir-ReO$_x$/SiO$_2$ catalyst and different acids for the selective production of *n*-pentane, pentanols or xylitol from hemicellulose (xylan) (Scheme 1).

2. Experimental

2.1. *Catalyst preparation*

Ir-ReO_x/SiO_2 catalysts were prepared by sequential impregnation method as described previously.[61-62, 65-74] First, Ir/SiO_2 was prepared by impregnating SiO_2 (Fuji Silysia G-6, calcined in air at 973 K for 1 h, BET surface area 535 m^2/g) with an aqueous solution of H_2IrCl_6 (Furuya Metals Co., Ltd). After evaporating the solvent at $\leq$ 353 K and drying at 383 K for 12 h, they were impregnated with an aqueous solution of NH_4ReO_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. The loading amount of Ir was 4.0 wt% and Re/Ir molar ratio was typically 2. All the catalysts were used in powdered form with a granule size of <100 mesh. HZSM-5 [JRC-Z5-90H(1), Süd-Chemie Catalysts and Catalysis Society of Japan, SiO_2/Al_2O_3 = 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. 0.5 g Xylan, an appropriate amount of H_2SO_4 aqueous solution and *n*-dodecane (0, 4 or 20 ml; Tokyo Chemical Industry Co. Ltd., 99%) were put into the autoclave. Three types of xylan were obtained from TCI, Wako and Sigma-Aldrich, and typically TCI-xylan was used. The elemental analysis results of these xylan samples are shown in Table S1 (ESI). 0.06 g HZSM-5 was also added when necessary. After sealing the reactor, the air content was purged by flushing three times with H_2 (1

MPa, 99.99%; Nippon Peroxide Co., Ltd.). The reactor was pressurized with H_2 to 6.0 MPa and then heated to set temperature (413 or 463 K). The heating took about 0.8 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 hydrogenolysis of xylitol (Wako Pure Chemical Industries, Ltd., 98%) was also tested in the similar way to the case of xylan.

The detected products were xylose, sugar alcohols: xylitol, arabitol, sorbitol; mono-alcohols: 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol, 2-hexanol and 3-hexanol; cyclic ethers: 2-methyltetrahydrofuran, tetrahydropyran and 2,5-dimethyltetrahydrofuran and alkanes: *n*-hexane, 2-methylpentane, 3-methylpentane, *n*-pentane, 2-methylbutane, cyclopentane, *n*-butane, propane, ethane and methane; and other products that could not be identified. Sugar and sugar alcohols in the aqueous phase were analyzed by using HPLC (Shimadzu LC-10A) with a refractive index detector (RID) and an Phenomenex Rezex RPM-Monosaccharide Pb+2 column (diameter 7.8 mm, 300 mm) and an Aminex HPX-87C column (diameter 7.8 mm, 300 mm). Mono-alcohols 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, 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. TC-WAX capillary column (diameter 0.25 mm, 30 m) and FID were used for separation of internal alcohols (2- and 3-pentanols) with the same carbon number. 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. The distributions of products in the three phases for typical runs are shown in Tables S2 and S3 (ESI).

The conversion of xylan and the yield of products were calculated on the carbon basis and defined as follows:

$$\text{Conversion [\%]} = \frac{\text{weight of xylan charged} - \text{weight of xylan after reaction}}{\text{weight of xylan charged}} \times 100$$

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

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

The weight of xylan after reaction was determined by subtracting the weight of the solid in the reaction mixture by the weight of catalysts. It should be noted that the formation of solid product on the catalysts underestimates the conversion value. Loss of carbon balance corresponds to the amount of polyols and soluble polymers. The used catalyst was washed with excess water and dried in air and then calcined at 773 K for 3 h. A slight loss (< 12% in weight) was observed during the recovery process and was compensated with fresh catalyst in each reuse experiment. The amount of eluted metal during the reaction and the amount of mineral ions in xylan were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Scientific iCAP 6500). X-ray diffraction (XRD) patterns of the used catalyst were recorded by a diffractometer (Rigaku MiniFlex 600).

3. Results and discussion

3.1 Production of n-pentane from xylan over Ir-ReO$_x$/SiO$_2$ + HZSM-5 + H$_2$SO$_4$ in biphasic solvent system

We chose Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) as the catalyst for hydrogenolysis because we have found that this catalyst is very effective in C-O hydrogenolysis of various molecules including cellulose.[61-62, 65-72] In our previous work, Ir-ReO$_x$/SiO$_2$ (Re/Ir=2) combined with HZSM-5 showed good performance in the production of *n*-hexane from ball-milled cellulose after 12 h reaction.[62] However, when this catalysts system was applied to conversion of xylan (TCI xylan), almost no *n*-pentane was formed even with prolonged reaction time (Table 1, entry 1). Large amount of humins were formed and deposited on the spinner and the wall of the reactor. The pH of filtrate after reaction was 6.94, which was almost neutral, while the filtrate of Ir-ReO$_x$/SiO$_2$ after reduction without xylan and even HZSM-5 had a pH value of 3.32. According to our previous work, Ir-ReO$_x$/SiO$_2$ catalyst was effective in C-O hydrogenolysis in acidic conditions[69]. The almost neutral condition not only decreases the activity of Ir-ReO$_x$/SiO$_2$ catalyst but also makes the hydrolysis rate of xylan into xylose lower. This could be the reason for the low yield of *n*-pentane and other detected products. In the production of hemicellulose, extraction with alkali was the most common method. Typically used alkalis are potassium, sodium and calcium hydroxide with the concentration of 0.05-0.15 g alkali / g biomass.[75] Some alkali could be converted to irrecoverable salts or incorporated as salts into hemicellulose samples.[74] Indeed, the used xylan contained small amount of Na^+ (11.66 mg / g xylan) and K^+ (0.14 mg / g xylan) (Table S1, ESI). The pH of the reaction solution and inorganic impurities could affect the activity of Ir-ReO_x/SiO_2.

To decrease the pH of reactant solution, different amount of H_2SO_4 was added. The yield of *n*-pentane increased and the pH value decreased quickly when the amount of H_2SO_4 was increased to 30 mg (Table 1, entries 1-4). The “conversion” of xylan was ≥ 94% for all entries, and the difference from 100% was probably due to the formation of solid product. This indicates that the C-O hydrogenolysis activity of Ir-ReO_x/SiO_2 catalyst is increased by decreasing the pH from ~7 to 2. Further increasing the amount of H_2SO_4, the pH of filtrate after reaction decreased slowly. The yield of *n*-pentane showed a volcanic type distribution when H_2SO_4 amount was further increased (Table 1, entries 4-8): The highest yield of *n*-pentane could reach about 70% when the added H_2SO_4 amount was 40~50 mg and the pH of filtrate was in the range of 1.65~1.82 (Table 1, entries 5-6). Further decreasing the pH of the filtrate (H_2SO_4 amount ≥ 60 mg) decreased the yield of *n*-pentane (Table 1, entries 7-8). The loss of carbon balance increased, which could be explained by formation of humins from xylan in strong acidic solution. The above results indicate that controlling the pH of the reactant solution is very important for production of *n*-pentane in high yield from xylan by using Ir-ReO_x/SiO_2 catalyst. It should be noted that when the reaction was conducted without xylan at 463

K for 24 h, no *n*-dodecane was converted. As a result, it is verified that the organic solvent is inert under the reaction conditions.

3.2 Time dependence on conversion of xylan to n-pentane

The time course of the reaction over Ir-ReO$_x$/SiO$_2$ + HZSM-5 with 40 mg H_2SO_4 was shown in Fig. 1. Almost all of the xylan was converted during the heating to 463 K. The main product just after heating was xylitol, which is the product of hydrolysis + hydrogenation of xylan. Then xylitol was further converted into *n*-pentane via polyols (undetected products = loss of carbon balance) and pentanols. The yield of *n*-pentane increased monotonously with reaction time. The yield of *n*-pentane reached about 70% when the most of detected oxygenates disappeared (24 h). These data support the reaction route shown in Scheme 1. First, H_2SO_4 and / or HZSM-5 hydrolyze xylan to xylose in hot water and then xylose is hydrogenated into xylitol over Ir-ReO$_x$/SiO$_2$ catalyst at the beginning of this reaction. Too low pH facilitates the formation of humins from xylan and decreases the amount of xylitol and the hydrogenolysis products. Next, hydrogenolysis of xylitol over Ir-ReO$_x$/SiO$_2$ and HZSM-5 in H_2SO_4 solution proceeds step by step to the end product of *n*-pentane. Although the reaction pathway of production of *n*-pentane from xylan was similar to that of production of *n*-hexane from cellulose, the rate-determining step was different: In the conversion of xylan, almost of all the xylan can be converted into xylitol at the beginning of the reaction and then xylitol was converted into *n*-pentane gradually. However, in the conversion of cellulose even after ball-milling, the conversion of cellulose and *n*-hexane yield is similar and the hydrolysis of cellulose into water-soluble sugars is the rate-determining step.[61] Xylan has a random, amorphous structure which is different from cellulose that has a robust crystalline structure, and xylan has lower degree of polymerization than cellulose. The addition of a small amount of H_2SO_4 could promote the hydrolysis rate of xylan, and the hydrolysis rate of xylan into xylose becomes faster than the hydrogenolysis rate of formed xylitol over Ir-ReO_x/SiO_2 catalyst. Under this situation, xylose can be converted to furfural by the acid catalyzed dehydration, and high concentration of furfural can give humins by the polymerization. Therefore, the rapid hydrogenation of xylose to xylitol is important in order to suppress the formation of furfural and subsequent polymerization to humins. Fortunately, it has been reported that Ir-ReO_x/SiO_2 catalyst has high activity in the hydrogenation of aldehyde,[72] which can contribute to the suppression of the reaction route via furfural. On the other hand, when xylitol was used as the substrate, over 60% yield of *n*-pentane can be produced in the same reaction system in only 0.5 h (Table 2, entries 1-4). The conversion of xylitol was much slower when it was in-situ produced from xylan (Fig. 1). To clarify the reason for this, two impacts were taken into consideration: the mineral substances in xylan and humins formed during the reaction.

3.3 The effect of mineral substance

In typical reaction conditions, 0.07 mg K^+ and 5.83 mg Na^+ derived from xylan were present in the reaction mixture (Table S1, ESI). Herein, to investigate the effect of K^+ and Na^+ on the catalytic performance, xylitol was chosen as the substrate, since xylitol is the primary intermediate in conversion of xylan. The K^+ and Na^+ precursors were K_2SO_4 and Na_2SO_4, respectively. The effect of

K^+ and Na^+ addition on the xylitol hydrogenolysis is shown in Table 2 (Table 2, entries 5-7 and 8-14, respectively). The yield of *n*-pentane decreased with increasing amount of Na^+ or K^+. The conversion of xylitol decreased below 90% when the amount of Na^+ was over 4.0 mg. The amount of loss of carbon balance, probably polyols, was increased. In our previous work, we found that two different hydrogenolysis mechanisms contributed to the last step of the production of *n*-pentane; i. e. hydrogenolysis of mono-alcohols.[50] The hydrogenolysis of 1-pentanol proceeds by direct hydrogenolysis catalyzed by Ir-ReO_x/SiO_2 while the hydrogenolysis of internal mono-alcohols (2- and 3-pentanol) proceeds by the dehydration + hydrogenation mechanism. The addition of HZSM-5 greatly accelerates the hydrogenolysis of internal mono-alcohols by promoting the dehydration. This can be supported by the higher yields of 2- and 3-pentanols over Ir-ReO_x/SiO_2 + H_2SO_4 without addition of HZSM-5 (Table 2, entries 4 and 21). Here, the yield of 1-pentanol increased as the amount of Na^+ or K^+ elevated from 0 mg to 0.6 mg. The amount of 2- and 3-pentanol remained small. These data indicate that Na^+ or K^+ mainly affected the direct hydrogenolysis pathway of Ir-ReO_x/SiO_2. Comparison between the data with similar K^+/Re or Na^+/Re molar ratio showed that K^+ has stronger deactivation effect (Table 2, entry pairs 6 and 8, 7 and 9). However, the K^+ content in xylan was much smaller than Na^+ and thus the effect by Na^+ could be much larger in xylan conversion. It was reported that the hydroxorhenium site (Re-OH) is the adsorption site of substrates which is very important for the direct C-O hydrogenolysis activity.[64-71] The addition of Na^+ or K^+ could decrease the number of hydroxorhenium site by ion exchange which decreases the catalytic activity (Scheme 2). Davis group has very recently reported that high concentration of sodium ions (100 mM NaCl) could poison the Pt-Re/C catalyst in the hydrogenolysis of glycerol by exchange with the acidic protons,[76] which could support our results. They also referred that the negative effect of Cl^- on Pt metal catalyst could also be inevitable.[75] On the other hand, the number of hydroxorhenium site can be increased by the addition of H_2SO_4 (Scheme 2) and the presence of hydroxo groups on the surface of the ReO_x clusters has been suggested by the characterization of Ir-ReO_x/SiO_2 by using Re L_3-edge-extended X-ray absorption fine structure (EXAFS) analysis.[64-71] Therefore, the effect of different amount of H_2SO_4 was investigated. The amount of Na^+ was fixed at 6 mg in the reaction solution which is almost the same in xylan conversion (Table 2, entries 11-18). Indeed, the yield of *n*-pentane increased when the amount of H_2SO_4 increased, especially with the pH value lower than 1.6. Comparison with the reaction tests without Na^+ (Table 2, entries 1-4) showed that the difference in *n*-pentane yield between runs with and without Na^+ shrinked by H^+ addition. This indicates that H^+ and Na^+ interact with Re site competitively (Scheme 2) and the addition of large amount of H_2SO_4 could increase the amount of active site (hydroxorhenium site (Re-OH)) that promoted hydrogenolysis activity of Ir-ReO_x/SiO_2 catalyst. However, even at pH < 1.4 (H_2SO_4 amount $\geq$ 40 mg), the yield of *n*-pentane was still lower in the presence of Na^+ or K^+. As discussed in section 3.1, too much H_2SO_4 (pH < 1.65) promotes the formation of humins and is not favorable in xylan conversion. The conversion of xylitol in Fig. 1, where xylitol was in-situ produced from xylan, was slowed down by the presence of Na^+ significantly. The amount of Na^+ content in xylan substrate can much affect the results.

We tested two other xylan samples. One was purchased from Wako, and it has similar amount of Na^+. The other one was purchased from Sigma-Aldrich, and it has slightly higher Na^+ content. The reaction results are shown in Table 3. Wako xylan showed almost the same yields as TCI xylan. On the other hand, Sigma-Aldrich xylan gave lower *n*-pentane yield than TCI xylan. Increasing the amount of H_2SO_4 from 40 mg to 50 mg increased the *n*-pentane yield from Sigma-Aldrich xylan to the comparable value to that obtained from TCI or Wako xylan. Therefore, adjusting the amount of H_2SO_4 for each xylan substrate is essential in obtaining good yield of *n*-pentane.

3.4 Catalyst stability

Table 4 shows the results of the activity tests of the reused $Ir\text{-}ReO_x/SiO_2$ (Re/Ir=2) + HZSM-5 catalysts. The method of the catalyst reuse was as follows: the solid catalysts ($Ir\text{-}ReO_x/SiO_2$ and HZSM-5) were recycled by centrifugation while H_2SO_4 in aqueous solution was discarded. The recycled solid catalysts were washed with water and dried at 383 K for 12 h and calcined in air at 773 K for 3 h. Before the activity test, the reduction pretreatment was carried out in the same way as the case of the fresh catalyst. The yield of *n*-pentane slightly decreased from 70% to 66% after four consecutive runs (Table 4, entries 1-4). Inductively coupled plasma (ICP) analysis of the reaction solution after the solid catalysts had been removed by filtration showed almost no Ir (<0.01%) and slight Re (0.92 wt%) leaching. The XRD peak patterns (ESI. Fig. S1) that were assigned to HZSM-5 were almost the same even after the fourth run while the peaks for Ir metal became sharper. The average size of Ir metal particle increased from 2.2 nm to 2.9 nm calculated by the Scherrer equation.[77] Therefore, the slight decrease of the yield of *n*-pentane and increase of the yields of cyclic ethers could be attributed to aggregation of metals during reaction and recalcination that lowered the hydrogenolysis activity of Ir-ReO_x/SiO_2 catalyst. It should be noted that the step of calcination is very important for the catalyst reuse. The yield of *n*-pentane dropped from 70% to 23% after the 1st reuse over the catalysts without calcination (Table 4, entries 1 and 5). The result of TG-DTA analysis showed that about 4 wt% humins (1.3 wt% based on the substrate) were formed on the solid catalysts after the first time reaction (ESI, Fig. S2a). The humins covered the active site of Ir-ReO_x/SiO_2 and HZSM-5 that led to the catalyst deactivation. To clarify the humins formed at the hydrolysis and hydrogenation step or the hydrogenolysis step, TG-DTA analysis was also performed by using the recovered solid catalysts after 0.5 h reaction (ESI, Fig. S2b). The amount of the humins was almost the same as that of the catalysts after 24 h reaction, indicating that the most of the humins were formed at the step of hydrolysis + hydrogenation of xylan. In addition, hydrogenolysis of xylitol over the catalysts after 0.5 h xylan reaction with calcination and without calcination was performed (ESI, Table S4). The yield of *n*-pentane was much lower over the catalysts without calcination compared to that over the fresh catalysts, while the yield of *n*-pentane was almost maintained over the catalysts with calcination. These results indicate that the humins formed at the beginning of conversion of xylan covered the active site of Ir-ReO$_x$/SiO$_2$ and HZSM-5 that decreased the hydrogenolysis performance.

3.5 Production of pentanols from xylan over Ir-ReO$_x$/SiO$_2$ + H$_2$SO$_4$ in biphasic solvent system

In our previous work, Ir-ReO$_x$/SiO$_2$ catalyst combined with H$_2$SO$_4$ was effective in the production of hexanols from mechanocatalytically depolymerized cellulose.[59] The keys to high hexanols yield are lowering reaction temperature, increasing cellulose reactivity (for such low reation temperature), and large amount of organic solvent for extraction. Here, we used Ir-ReO$_x$/SiO$_2$ + H$_2$SO$_4$ and larger amount of *n*-dodecane (20 ml) for conversion of xylan into pentanols at lower reaction tempeatrue (413 K). The effect of H$_2$SO$_4$ amount was investigated and the results are shown in Table 5. The yield of pentanols showed a volcanic type distribution when the amount of H$_2$SO$_4$ was in the range of 30~60 mg (Table 5). The main products were 2-pentanol and 3-pentanol. Large amount of polyols still existed when the amount of H$_2$SO$_4$ was 30 mg (Table 5, entry 1), reflected by the low C-O hydrogenolysis activity of Ir-ReO$_x$/SiO$_2$ under this reaction condition. The yield of *n*-pentane increased as the addition of H$_2$SO$_4$ increased, indicating that over-hydrogenolysis proceeded at lower pH (Table 5, entries 1-4). It was reported that hydrogenolysis of 2- and 3-pentanols proceeds by the tandem dehydration and hydrogenation mechanism.[50] The lower pH facilitated the dehydration of 2- and 3-pentanols thereby further hydrogenated to *n*-pentane over Ir-ReO$_x$/SiO$_2$ (ESI, Table S5). The yield of pentanols could reach about 32% when the added H$_2$SO$_4$ amount was 40~50 mg (Table 5, entries 2-3). The time course of the reaction was shown in Table S6 (ESI), and the highest yield of pentanols was obtained at this reaction time. The above results indicate that controlling the acidity of the reactant solution is also very important for production of pentanol in high yield from xylan by using Ir-ReO_x/SiO_2 catalyst, and the optimum H_2SO_4 amount is similar to that in *n*-pentane production. The production of pentanols from other xylan was also tested (Table 5, entries 5-7). Similarly to *n*-pentane production, the yield of pentanols from Wako xylan was almost the same as that from TCI xylan. The yield of pentanols from Sigma-Aldrich xylan was lower than those from TCI or Wako xylans, and it was increased to a comparable value by adjusting the H_2SO_4 amount.

3.6 Production of xylitol from xylan over Ir-ReO_x/SiO_2 + H_2SO_4 in aqueous phase

At the beginning of the reactions in production of *n*-pentane or pentanols from xylan, over 60% yield of xylitol was obtained, which motivated us to convert xylan to xylitol in high yield. To obtain higher yield of xylitol, protection of the formed xylitiol from hydrogenolysis into other products is the key. Two ways can be applied for this. The first one is lowering the reaction temperature with short reaction time. The other one is decreasing the amount of H_2SO_4 to decrease the number of the hydroxorhenium site (Re-OH). In the production of xylitol, only water was used as a solvent because xylitol is soluble in water. The results were shown in Table 6. First, the effect of H_2SO_4 amount was investigated (Table 6, entries 1-4). The yield of xylitol increased quickly with the amount of H_2SO_4 elevating from 10 to 30 mg, indicating the importance of H_2SO_4 for hydrolysis of xylan. Further increase in the amount of H_2SO_4 slightly decreased the yield of xylitol, which can be attributed to the hydrogenolysis reaction. Next, the effect of reaction temperature was also investigated (Table 6, entries 6-9). The loss of carbon balance was higher at lower reaction temperature (Table 6, entry 6), which can be explained by the low hydrolysis rate. The yield of arabitol was higher at higher reaction temperature, indicating that the isomerization reaction proceeded. The highest yield of xylitol could reach 79% when the reaction temperature was 403 K (Table 6, entry 7). The performances of different commercial noble metals on carbon catalysts (Ru/C, Pt/C, Rh/C and Pd/C) were compared with that of Ir-ReO_x/SiO_2 (ESI, Table S7). The yield of xylitol (≤ 61%) was lower than that of over Ir-ReO_x/SiO_2 catalyst (79%). In the case of Pd/C, the yield of xylitol was higher than other carbon-supported noble metal catalysts; however, it is still lower than that over Ir-ReO_x/SiO_2. The 13% yield of xylose on Pd/C can be explained by the lower hydrogenation activity of Pd/C than that of Ir-ReO_x/SiO_2, which is also supported by our previous work that Ir-ReO_x/SiO_2 has high activity of the hydrogenation of formyl group in unsaturated aldehydes.[73] In the case of Ru/C, very low yield of xylose indicates that Ru/C has high hydrogenation activity of xylose, however, the side reaction of the isomerization of xylitol to arabitol proceeds and this can decrease the yield of xylitol significantly. This behavior is explained by the high ability of Ru/C in the dehydrogenation of CH-OH because the isomerization reaction proceeds in dehydrogenation + hydrogenation route and at the same time, these tendencies indicate that Ir-ReO_x/SiO_2 has much lower isomerization activity, which is connected to high xylitol yield on Ir-ReO_x/SiO_2. The very low isomerization activity of Ir-ReO_x/SiO_2 and the high isomerization performance of Ru/C are also supported in the case of the hydrogenolysis of erythritol.[68] In the cases of Pt/C and Rh/C, the yield of xylose was high, which means the low activity of these catalysts in hydrogenation of xylose. As a result, it is concluded that Ir-ReO$_x$/SiO$_2$ is very efficient for the production of xylitol by hydrolysis + hydrogenation of xylan.

The production of xylitol from other xylan was also tested (Table 7). In contrast to the cases of *n*-pentane or pentanols productions, all the three xylans can be converted to xylitol in similar high yield. The active site of the hydrogenation is suggested to be the interface between Ir metal and ReO$_x$ species,[73] and the substrate is probably coordinated to Re atom with the oxygen atom in the C=O bond. The number of hydroxorhenium site may not affect the activity.

4. Conclusions

Ir-ReO$_x$/SiO$_2$ combined with acids was very effective in conversion of hemicellulose (xylan) into three different products, *n*-pentane, pentanols and xylitol, by simply adjusting the reaction temperature, amounts of organic solvent and reaction time. 70% yield of *n*-pentane can be produced by using Ir-ReO$_x$/SiO$_2$ combined with HZSM-5 + H_2SO_4 in biphasic solvent system (4 ml *n*-dodecane + 9.5 ml H_2O) at 463 K for 24 h. 32% yield of pentanols can be produced by using Ir-ReO$_x$/SiO$_2$ combined with H_2SO_4 in biphasic solvent system (20 ml *n*-dodecane + 9.5 ml H_2O) at 413 K for 144 h. 79% yield of xylitol can be produced by using Ir-ReO$_x$/SiO$_2$ combined with H_2SO_4 in aqueous phase at 413 K for 12 h. Adjusting the amount of H_2SO_4 is also very important, and especially for *n*-pentane or pentanols production. The optimum amount of H_2SO_4 depended on the amount of mineral ions in the xylan samples.

The conversion of xylan and the yield of *n*-pentane were almost maintained during three repeated tests when the catalyst was calcined during the regeneration procedure. The humins, formed at the hydrolysis + hydrogenation step during xylan conversion, covered the active site of Ir-ReO_x/SiO_2 and HZSM-5 to decrease C-O hydrogenolysis performance of Ir-ReO_x/SiO_2 in part. The calcination step for removing the humins is very important for the catalyst reuse.

The mineral ions (such as Na^+ and K^+) in xylan also decrease C-O hydrogenolysis performance of Ir-ReO_x/SiO_2 catalyst severely because the mineral ions decreased the number of active site of Ir-ReO_x/SiO_2 (hydroxorhenium site (Re-OH)) by ion exchange. The addition of H_2SO_4 not only kept the acidic reaction environment, which is beneficial for the Ir-ReO_x/SiO_2 catalyst works, by neutralizing the residual alkali of xylan after being isolated from lignocellulose, but also maintained and enhanced the C-O hydrogenolysis activity of Ir-ReO_x/SiO_2 through increasing the amount of hydroxorhenium site by the competitive adsorption of proton on Re site with mineral ions. However, too much amount of H_2SO_4 decreased the yields of target compounds by humins formation from xylan and / or overhydrogenolysis.

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Table 1 Conversion of xylan to *n*-pentane over Ir-ReO$_x$/SiO$_2$ + HZSM-5 catalysts with different amount of H_2SO_4

Entry	H_2SO_4 / mg	Conversion / %	Yield / %								Loss of carbon balance	pH
			n-Pentane	Other pentanes	*n*-Hexane	Other hexanes	Cyclic ethers	PeOHs	HxOHs	C1-C4 alkanes		
1	0	95	3.0	0.2	2.1	0.0	0.0	0.0	0.0	2.9	86	6.94
2	10	94	1.0	0.4	0.0	0.0	0.5	4.2	0.1	1.2	86	5.85
3	20	94	6.3	0.6	0.6	0.1	1.3	15	2.0	3.8	65	4.64
4	30	96	64	1.2	5.9	0.5	1.4	0.6	0.0	6.4	17	2.04
5	40	98	70	2.5	7.3	0.9	0.8	0.9	0.0	5.2	10	1.82
6	50	95	70	3.2	7.4	0.7	3.9	0.0	0.0	5.8	4.2	1.65
7	60	97	62	2.9	7.8	0.7	3.2	0.0	0.3	4.2	16	1.45
8	70	97	57	2.9	7.0	0.6	3.4	0.2	0.3	4.2	21	1.34

Other hexanes: 2-methylpentane and 3-methylpentane, Other pentanes: 2-methylbutane and cyclopentane, HxOH: Hexanol; PeOH: Pentanol; cyclic ethers: 2-methyltetrohydrofuran, tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran; C1-C4 alkanes: methane, ethane, propane and *n*-butane. Sugars and sugar alcohols were not detected in all entries.

Reaction conditions: TCI xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO$_x$/SiO$_2$: 0.15 g, HZSM-5: 0.06 g, *n*-dodecane: 4 ml, 463 K, initial H_2: 6 MPa, 24 h.

Table 2 The effect of K^+, Na^+ and H^+ on Ir-ReO_x/SiO_2 + HZSM-5 catalysts for conversion of xylitol to *n*-pentane

Entry	Additive / mg			pH	Molar Ratio		Conversion / %	Yield / %						Loss of carbon balance
	K^+	Na^+	H_2SO_4		(K^+ or Na^+)/Re	H_2SO_4/(Na^+ or K^+)		*n*-Pentane	Other pentanes	Cyclic ethers	1-PeOH	2- and 3-PeOH	C1-C4 alkanes	
1	0	0	0	2.99	-	-	>99	52	0.6	8.3	6.6	1.8	2.3	28
2	0	0	10	1.88	-	-	>99	63	0.5	7.4	4.2	1.0	2.5	21
3	0	0	20	1.59	-	-	>99	68	0.6	7.4	2.9	0.9	2.9	18
4	0	0	40	1.30	-	-	>99	74	1.2	7.1	2.6	0.0	2.7	12
5	0.2	0	0	2.99	0.08	-	>99	49	0.4	7.9	6.8	2.4	2.3	31
6	0.4	0	0	2.90	0.16		>99	45	0.3	8.0	9.4	2.7	2.2	33
7	0.6	0	0	2.93	0.25		>99	27	0.2	6.3	11	2.7	1.4	52
8	0	0.2	0	2.89	0.14	-	>99	52	0.4	7.6	7.0	2.0	2.6	28
9	0	0.4	0	2.88	0.28	-	>99	45	0.3	7.3	9.0	3.2	2.2	33
10	0	1.0	0	3.11	0.70	-	>99	15	0.0	3.0	4.9	5.4	1.1	71
11	0	2.0	0	3.11	1.4	-	>99	4.9	0.0	2.4	7.0	5.8	0.7	79
12	0	4.0	0	3.02	2.8	-	83	2.5	0.0	0.3	2.1	3.0	0.5	75
13	0	6.0	0	3.02	4.2	-	80	2.0	0.0	0.0	1.3	2.5	0.5	74
14	0	8.0	0	2.94	5.6	-	73	1.1	0.0	0.0	0.9	1.8	0.3	69
15	0	6.0	5	2.13	4.2	0.20	>99	6.0	0.0	1.8	4.0	4.5	0.7	83
16	0	6.0	10	1.89	4.2	0.39	>99	12	0.1	3.1	6.1	3.5	0.8	74
17	0	6.0	20	1.61	4.2	0.8	>99	42	0.3	6.7	8.9	2.0	1.8	38
18	0	6.0	40	1.39	4.2	1.5	>99	63	0.8	7.1	3.3	0.9	2.4	23
19	0	6.0	60	1.24	4.2	2.4	>99	63	0.7	6.7	3.6	0.6	2.5	23
20	0.6	0	40	1.36	0.25	27	>99	63	0.7	8.0	6.4	2.2	2.2	17
21[a]	0	0	40	1.32	-	-	>99	56	0.1	3.8	3.6	8.3	1.4	27

Other hexanes: 2-methylpentane and 3-methylpentane, Other pentanes: 2-methylbutane and cyclopentane, HxOH: Hexanol; PeOH: Pentanol; cyclic ethers: 2-methyltetrohydrofuran, tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran; C1-C4 alkanes: methane, ethane, propane and *n*-butane.

Reaction conditions: xylitol: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, HZSM-5: 0.06 g, additive: Na_2SO_4, K_2SO_4 and/or H_2SO_4, *n*-dodecane: 4 ml, 463 K, initial H_2: 6 MPa, 0.5 h, a: without HZSM-5.

Table 3 Conversion of different xylan to *n*-pentane over Ir-ReO_x/SiO_2 + HZSM-5 catalysts with different amount of H_2SO_4

Entry	Xylan	Na^+ / $mg_{Na+}\cdot g^{-1}_{xylan}$	K^+ / $mg_{K+}\cdot g^{-1}_{xylan}$	Conversion / %	Yield / %								Loss of carbon balance	pH
					n-Pentane	Other pentanes	*n*-Hexane	Other hexanes	Cyclic ethers	PeOHs	HxOHs	C4-C1 alkanes		
1	TCI	11.66	0.14	98	70	2.5	7.3	0.9	0.8	0.9	0.0	5.2	10	1.82
2	Wako	11.33	0.15	96	69	1.6	6.9	0.9	1.1	0.0	0.0	5.3	11	1.86
3	Sigma-Aldrich	13.59	0.17	95	54	2.0	4.3	0.3	0.7	0.0	0.0	5.6	28	2.15
4[a]	Sigma-Aldrich	13.59	0.17	96	66	2.5	7.4	1.0	1.8	0.0	0.0	4.2	13	1.85

Other hexanes: 2-methylpentane and 3-methylpentane, Other pentanes: 2-methylbutane and cyclopentane, HxOH: Hexanol; PeOH: Pentanol; cyclic ethers: 2-methyltetrohydrofuran, tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran; C1: methane; C2: ethane; C3: propane; C4: *n*-butane;

Reaction conditions: xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, HZSM-5: 0.06 g, H_2SO_4: 40 mg, *n*-dodecane: 4 ml, 463 K, initial H_2: 6 MPa, 24 h, a: H_2SO_4 50 mg.

Table 4 Reusability of Ir-ReO$_x$/SiO$_2$ + HZSM-5 catalysts for conversion of xylan to *n*-pentane

Entry	Usage	Conversion / %	Yield / %								Loss of carbon balance
			n-Pentane	Other pentanes	*n*-Hexane	Other hexanes	Cyclic ethers	PeOHs	HxOHs	C4-C1 alkanes	
1	1	98	70	2.5	7.3	0.9	0.8	0.9	0.0	5.2	10
2	2	97	69	2.3	7.0	0.7	1.6	1.1	0.2	5.3	9.8
3	3	>99	67	2.7	6.1	0.4	4.3	0.0	0.4	5.2	14
4	4	97	66	2.7	6.0	0.4	4.6	0.1	0.3	4.9	12
5	2[a]	99	23	1.3	1.9	0.0	5.9	7.3	0.7	1.3	57

Other hexanes: 2-methylpentane and 3-methylpentane, Other pentanes: 2-methylbutane and cyclopentane, HxOH: Hexanol; PeOH: Pentanol; cyclic ethers: 2-methyltetrohydrofuran, tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran; C1-C4 alkanes: methane, ethane, propane and *n*-butane.

Reaction conditions: TCI xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO$_x$/SiO$_2$: 0.15 g, HZSM-5: 0.06 g, H_2SO_4: 40 mg, *n*-dodecane: 4 ml, 463 K, initial H_2: 6 MPa, 24 h, a: without calcination before reuse.

Table 5 Conversion of xylan to pentanols over Ir-ReO_x/SiO_2 catalyst + H_2SO_4

Entry	H_2SO_4 / mg	Conversion / %	Yield / %									Loss of carbon balance	pH
			Sum of PeOHs	1-PeOH	2-PeOH	3-PeOH	HxOHs	Pentanes	Hexanes	C1-C4 alkanes	Cyclic ethers		
1	30	97	20	3.4	7.0	9.9	2.4	6.9	0.8	1.2	0.7	64	2.05
2	40	95	32	1.3	13	17	3.7	22	1.7	1.8	2.0	33	1.83
3	50	97	32	0.3	14	18	4.4	30	2.3	1.9	2.2	24	1.66
4	60	94	22	0.3	9	12	4.8	42	3.5	1.8	2.6	18	1.57
5[a]	40	97	31	0.7	15	16	3.9	22	1.7	1.8	1.9	35	1.79
6[b]	40	97	20	5.5	7.3	6.7	2.6	7.9	0.7	0.9	1.4	64	1.87
7[b]	50	96	29	0.4	12	16	3.7	26	2.0	1.4	1.9	33	1.71

PeOH: Pentanol; HxOH: Hexanol; Pentanes: *n*-pentane, 2-methylbutane and cyclopentane, Hexanes: *n*-hexane, 2-methylpentane and 3-methylpentane, C1-C4 alkanes: methane, ethane, propane and *n*-butane; cyclic ethers: 2-methyltetrohydrofuran, tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran;
Reaction conditions: TCI xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO_x/SiO_2: 0.15 g, *n*-dodecane: 20 ml, 413 K, initial H_2: 6 MPa, 144 h, a: Wako xylan, b: Sigma-Aldrich xylan.

Table 6 Conversion of xylan to xylitol over Ir-ReO$_x$/SiO$_2$ catalyst + H_2SO_4

Entry	H_2SO_4 / mg	T / K	Conversion / %	Yield / %				Loss of carbon balance	pH
				Xylitol	Arabitol	Sorbitol	Alkanes		
1	10	413	92	18	0.6	0.3	0.1	72	4.42
2	15	413	92	47	0.9	0.7	0.2	43	4.01
3	20	413	92	74	0.8	1.3	0.4	16	3.01
4	30	413	93	78	1.0	2.4	0.5	11	2.17
5	40	413	91	73	1.0	3.4	0.6	13	1.87
6	30	393	94	74	0.6	1.0	0.1	18	2.17
7	30	403	97	79	0.8	2.3	0.1	15	2.17
8	30	423	93	75	1.3	2.9	0.3	13	2.17

Alkanes: C1-C6 alkanes.

Reaction conditions: TCI xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO$_x$/SiO$_2$: 0.15 g, initial H_2: 6 MPa, 12 h.

Table 7 Conversion of different xylan to xylitol over Ir-ReO$_x$/SiO$_2$ catalyst + H_2SO_4

Entry	Xylan	Conversion / %	Yield / %				Loss of carbon balance	pH
			Xylitol	Arabitol	Sorbitol	Alkanes		
1	TCI	93	78	1.0	2.4	0.5	11	2.17
2	Wako	92	77	0.9	2.4	0.2	11	2.26
3	Sigma-Aldrich	93	78	0.2	2.1	0.1	13	2.36

Alkanes: C1-C6 alkanes.

Reaction conditions: xylan: 0.5 g, H_2O: 9.5 g, Ir-ReO$_x$/SiO$_2$: 0.15 g, H_2SO_4: 30 mg, initial H_2: 6 MPa, 413 K, 12 h.

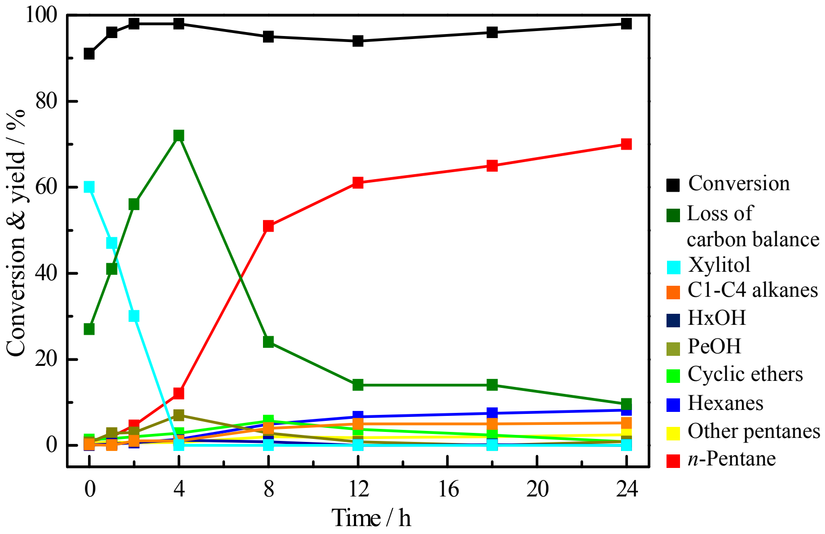
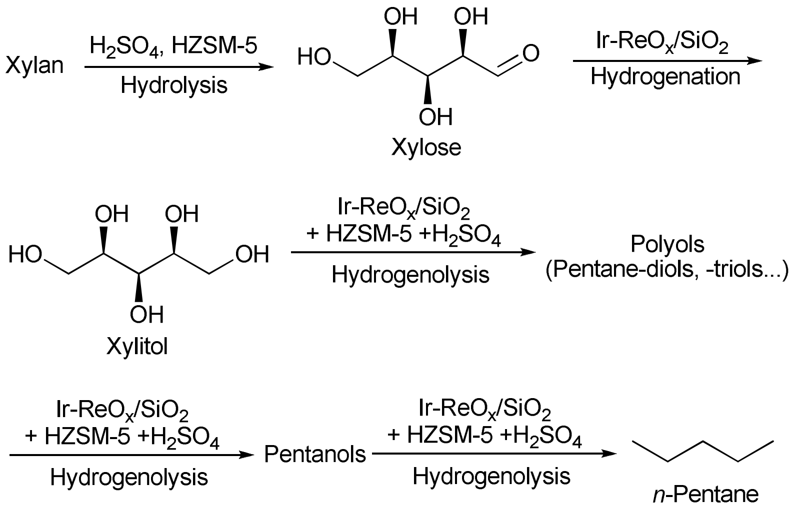
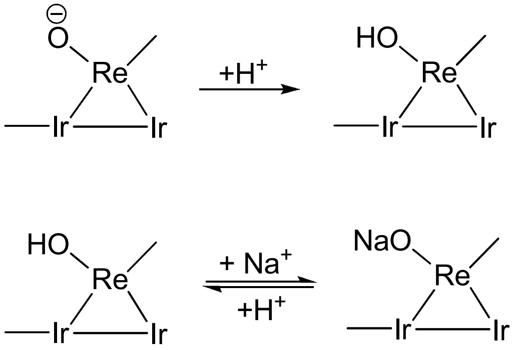


Fig. 1. Time dependence of conversion of xylan to *n*-pentane over Ir-ReO$_x$/SiO$_2$ + HZSM-5 + H$_2$SO$_4$
Reaction conditions: TCI Xylan: 0.5 g, H$_2$O: 9.5 g, Ir-ReO$_x$/SiO$_2$: 0.15 g, HZSM-5: 0.06 g, H$_2$SO$_4$: 40 mg, *n*-dodecane: 4 ml, 463 K, initial H$_2$: 6 MPa.



Scheme 1. The reaction pathway for conversion of xylan to *n*-pentane over Ir-ReO_x/SiO_2 + HZSM-5 + H_2SO_4



Scheme 2. The formation of hydroxorhenium site and ion-exchange with Na^+ or H^+

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n-Pentane (yield 70%), pentanols (32%) or xylitol (79%) can be produced from xylan by using Ir-ReO_x/SiO_2 catalyst combined with acids.