

## Investigation on the xylitol aqueous-phase reforming performance for pentane production over Pt/HZSM-5 and Ni/HZSM-5 catalysts

Ting Jiang<sup>a,b,\*</sup>, Tiejun Wang<sup>a</sup>, Longlong Ma<sup>a,\*</sup>, Yuping Li<sup>a</sup>, Qing Zhang<sup>a</sup>, Xinghua Zhang<sup>a</sup>

<sup>a</sup> Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, China

<sup>b</sup> Graduate School of Chinese Academy of Sciences, Beijing, China

### ARTICLE INFO

#### Article history:

Received 29 September 2010

Received in revised form 22 March 2011

Accepted 23 March 2011

Available online 6 May 2011

#### Keywords:

Aqueous-phase reforming

Alkane production

Xylitol

Ni/HZSM-5

Pt/HZSM-5

### ABSTRACT

Pt/HZSM-5 and Ni/HZSM-5 catalysts were prepared and evaluated for aqueous-phase reforming (APR) reaction of xylitol. Effects of reaction temperature, pressure and metal loading on xylitol conversion and pentane selectivity were studied. Experiments over 4 wt% Pt/HZSM-5 catalysts showed that high temperature increased the xylitol conversion while high pressure led to the decrease of pentane selectivity. The xylitol conversion and pentane selectivity increased with the metal loading in the range of 0–3 wt%, but the values decreased as further increasing the metal loading to 5 wt% over both Ni/HZSM-5 and Pt/HZSM-5, indicating that higher metal loading would increase the rate of C–C bond cleavage compared to hydrogenation. Under the condition of 240 °C and 4 MPa, Ni/HZSM-5 and Pt/HZSM-5 with the same metal loading of 2 wt% showed similar xylitol conversion, while the primary had higher pentane selectivity of 95% than 58% of the latter. Ni has higher activity for pentane production than Pt during the APR reaction of xylitol, while Pt has stronger effect of C–C bond cleavage to produce lighter alkanes of C<sub>1</sub>–C<sub>4</sub>. In order to investigate catalyst recyclability, 2 wt% Ni/HZSM-5 was reused and analyzed by TG characterization. It was found that considerable amount of coke and heavy hydrocarbons were formed on the catalyst surface, which could cover the active sites and cause catalyst deactivation.

© 2011 Elsevier Ltd. All rights reserved.

### 1. Introduction

The declining fossil reserves urge us to develop economical and energy-efficient process for the production of fuels from renewable resources. Biomass represents a potential alternative source of liquid fuels and chemicals, because it is an abundant, renewable source of carbon-containing molecules [1,2]. The high water solubility of biomass-derived carbohydrates, due to the high oxygen content, make aqueous-phase processing of these compounds an attractive step [3]. Recently, Dumesic and co-workers proposed a catalytic approach to produce alkanes by aqueous-phase reforming (APR) reaction from biomass-derived carbohydrates such as sugars and sugar alcohols, which can be obtained from the lignocellulosic biomass by hydrolysis and hydrogenation [4–7]. Since APR process can be accomplished in a single reaction vessel and alkane products can be easily separated from water, the overall thermal efficiency can be improved by avoiding energy-intensive distillation/purification steps [2,8]. These works highlighted the possibility of producing gasoline from renewable biomass resources, thus attracting much attention from researchers [9].

Previous studies demonstrated that sorbitol could be converted to C<sub>1</sub> to C<sub>6</sub> straight-chain alkanes by APR reaction over bifunctional catalysts, which contain acid and metal sites to catalyze dehydration and hydrogenation reactions respectively [10]. The sorbitol APR reaction for alkane production involves first C–O bond cleavage by dehydration on acid sites, then the dehydrated intermediates migrate to metal sites where they undergo hydrogenation reactions [11]. However, the APR process is very complex and many side reactions may also occurred over the bifunctional catalysts, such as C–C bond cleavage reactions and F–T synthesis [12]. The yield of gasoline-range alkanes (C<sub>5</sub>–C<sub>13</sub>) was also less than 60 carbon% [13]. Large amounts of by-products such as ketones and acids cannot be used directly before further upgrading [14]. A variety of supports were tested to adjust the acid strength for dehydration (SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, ZrP, etc.), and the metal used for hydrogenation were usually noble metal with high loadings amount such as 4–5 wt% Pt and 5 wt% Re [3,13,15,16]. Little work has been carried out so far in optimizing the metal composition [17]. Moreover, less research was focused on the APR reaction of C<sub>5</sub> sugars, which contain up to 30 wt% in lignocellulose biomass and were difficult to be used in biological fermentation process [18].

In this paper, production of pentane by APR reaction over Pt/HZSM-5 catalysts from C<sub>5</sub> carbohydrates of xylitol was

\* Corresponding author. Tel.: +86 20 87057751.

\*\* Presenting author. Tel.: +86 20 87057787.

E-mail addresses: [jiangting@ms.giec.ac.cn](mailto:jiangting@ms.giec.ac.cn) (T. Jiang), [mall@ms.giec.ac.cn](mailto:mall@ms.giec.ac.cn) (L. Ma).

investigated. To reduce the catalyst cost, less expensive Ni was also used as the metal catalyst due to its excellent hydrogenation activity. The effects of reaction temperature, pressure, and metal loadings were studied on the xylitol conversion and pentane selectivity. The reaction pathways were also discussed to explain how the APR process can be designed to produce desired alkanes by adjusting the relative rate of C–C vs. C–O bond cleavage.

## 2. Experimental

### 2.1. Catalyst preparation

Pt/HZSM-5 and Ni/HZSM-5 catalysts were prepared by wet impregnation of aqueous solutions of platinum chloride ( $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ ) or nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) over HZSM-5 support (BET:  $230 \text{ m}^2/\text{g}$ , pore volume:  $0.01 \text{ cm}^3/\text{g}$ , pore diameter:  $0.7 \text{ nm}$ , Si/Al = 38). The metal loadings of Pt/HZSM-5 or Ni/HZSM-5 catalysts were 1, 2, 3, 4 wt%, respectively. The suspension was stirred at  $70 \text{ }^\circ\text{C}$  for 6 h, dried at  $120 \text{ }^\circ\text{C}$  for 12 h and then calcined in air at  $550 \text{ }^\circ\text{C}$  for 3 h. Prior to reaction, all the catalysts were reduced in 5%  $\text{H}_2/\text{N}_2$  flow of  $100 \text{ ml}/\text{min}$  at  $450 \text{ }^\circ\text{C}$  for 3 h.

### 2.2. Product analysis and catalyst characterization

Gas products were analyzed by two off-line gas chromatographs. Alkanes ( $\text{C}_1\text{--}\text{C}_6$ ) were analyzed by Porapak Q column with FID detector (Shimadzu GC2010).  $\text{CO}_2$  were analyzed by carbon-sieve column with TCD detector.

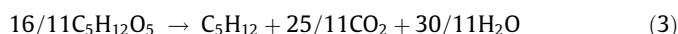
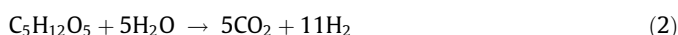
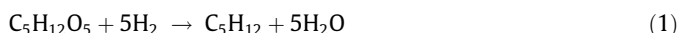
X-ray powder diffraction (XRD) patterns were obtained on a RigakuD/max-rC using Cu Ka ( $\lambda = 0.15406 \text{ nm}$ ) radiation. TG studies of used catalysts were carried out under an air flow rate of  $30 \text{ ml}/\text{min}$  by STA409PC from  $40 \text{ }^\circ\text{C}$  to  $900 \text{ }^\circ\text{C}$  at the heating rate of  $15 \text{ }^\circ\text{C}/\text{min}$ .

### 2.3. Experimental methods and data processing

The APR reactions of xylitol were carried out in a  $100 \text{ ml}$  stainless autoclave equipped with an electromagnetic driven stirrer. The schematic diagram is shown in Fig. 1. For each run,  $3.0 \text{ g}$  xylitol,  $50 \text{ ml}$  water and  $3.0 \text{ g}$  catalyst were loaded in the autoclave. After displacing air, the  $\text{H}_2$  pressure was raised to  $2.0\text{--}4.0 \text{ MPa}$ . The reaction temperature was changed from  $180 \text{ }^\circ\text{C}$  to  $250 \text{ }^\circ\text{C}$ . Reagents were vigorously stirred (500 rotations per minute) in order to

eliminate the diffusion limitation. The gas products from the reactor flowed through a back pressure regulator, which was used to maintain the pressure of the reaction system. Each test lasts 4 h including the heating time. The cumulate gas efflux was measured when desired reaction temperature was achieved. Tail gas collected was sampled into gas bag every 15 min for off-line gas chromatography (GC) analysis.

The stoichiometry for the conversion of xylitol to pentane can be considered as the reduction of xylitol to pentane combined with the aqueous-phase reforming of xylitol to  $\text{H}_2$  and  $\text{CO}_2$ , as given by Eqs. (1) and (2). Hydrogen could be produced in the catalytic process near  $500 \text{ K}$  from APR of xylitol in the same reactor, which would supply  $\text{H}_2$  for the reduction reaction. The overall reaction Eq. (3) is an exothermic process in which 88% of the heating value of the xylitol reactant is retained in the pentane product.



The carbon balance estimated by the sum of alkane products,  $\text{CO}_2$  and unreacted xylitol vs. fed xylitol are about 90–99% in most cases. The mass loss would be ascribed to the formation of polymers or/and cokes during the reaction processes and undetectable liquid by-products. Main products of aqueous-phase catalytic hydrogenation/dehydration of xylitol are  $\text{C}_1\text{--}\text{C}_6$  alkanes, and pentane is the target product. For the convenience of subsequent discussion, xylitol conversion and alkane selectivity are calculated based on moles of carbon atoms in xylitol or alkanes, as shown in the definition formulas listed below [13]:

$$\text{Xylitol conversion \%} = \frac{\sum_{i=1}^6 i \times \text{molesC}_i + \text{moleCO}_2}{5 \times \text{moleXylitolfed}} \times 100 \quad (4)$$

$$\text{Alkane selectivity \%} = \frac{i \times \text{moleC}_i}{\sum_{i=1}^6 i \times \text{molesC}_i} \times 100 \quad (5)$$

In the formulas (4) and (5),  $i$  is the carbon atom numbers for alkanes;  $\text{C}_i$  is the alkane which contains carbon atom numbers of  $i$ .

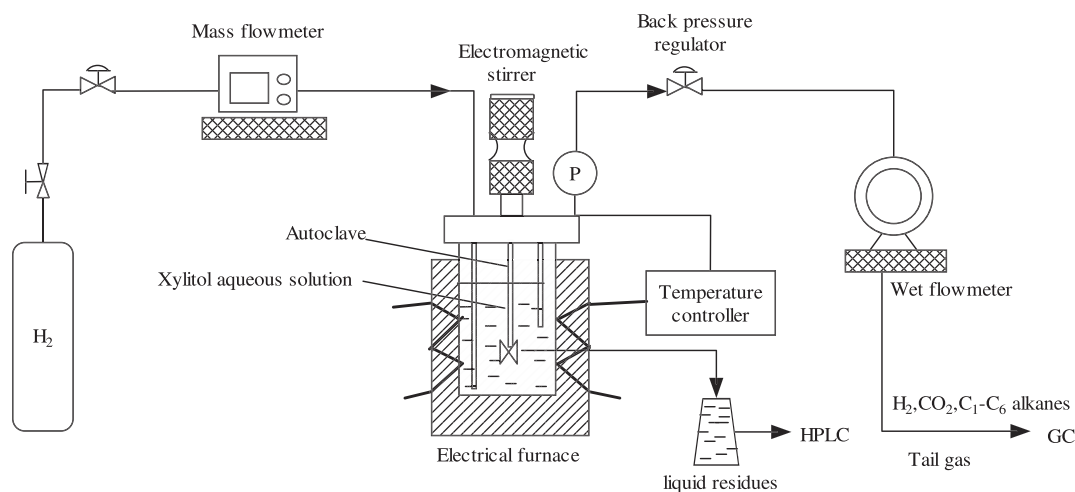


Fig. 1. The experimental apparatus for the APR reaction of xylitol.

Download English Version:

<https://daneshyari.com/en/article/243903>

Download Persian Version:

<https://daneshyari.com/article/243903>

[Daneshyari.com](https://daneshyari.com)