Aqueous-phase catalytic process for production of pentane from furfural over nickel-based catalysts

Zhang Xinghua [a,b], Wang Tiejun [a,*], Ma Longlong [a], Wu Chuangzhi [a]

[a] Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, Guangdong 510640, PR China
[b] Graduate School of Chinese Academy of Science, Beijing 100049, PR China

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ABSTRACT

Supported nickel catalysts for aqueous-phase catalytic hydrogenation/dehydration of furfural were prepared using impregnation method with different supporting materials. Effects of supporting materials, nickel loading and reaction temperature on conversion rate of furfural as well as selectivity for desired product C_5 were systematically studied. Experiments showed that catalytic activity of $Ni/SiO_2–Al_2O_3$ was obviously higher than that of Ni/γ-Al_2O_3. The conversion of furfural over 14 wt.%$Ni/SiO_2–Al_2O_3$ catalyst was 62.99% under the temperature of 140 °C and the cold pressure of H_2 3.0 MPa, while that was 19.19% over 14 wt.%Ni/γ-Al_2O_3 under the same conditions. Conversion rate of furfural increased with temperature, but selectivity for desired product decreased with temperature. Tentative reaction mechanisms of hydrogenation/dehydration were proposed. In order to investigate catalyst recyclability, a batch of $Ni/SiO_2–Al_2O_3$ was reused three times and analyzed by Thermogravimetry (TG). It was found that considerable amount of coke formed on $Ni/SiO_2–Al_2O_3$ surface and deteriorated its activity dramatically after second use.

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1. Introduction

Biomass offers a sustainable resource for the future. It has the potential advantages in alleviating environmental pollution, slowing global warming, and reducing our dependence on the limited fossil fuels [1]. Especially in recent years, with the increasing price of oil, it is necessary to develop some feasible processes to produce liquid fuels from non-petroleum resources. One of the dramatic strategies for replacing petroleum fuels in the transportation sector is developing biomass-derived liquid fuels, which utilizes the existing delivery infrastructure while no extensive vehicle engine modification is needed [2]. Recently, Dumesic proposed a new scheme to produce alkanes from biomass-derived carbohydrates by aqueous-phase reforming reaction, which could be used as clean diesel fuel for transportation applications [3–5]. Because the process can be accomplished in a single reaction vessel and the products can be separated spontaneously from water, aqueous-reforming of renewable carbohydrates is attractive.

Furan compounds such as furfural, methyl furfural and hydroxymethylfurfural (HMF) can be produced with good yields though catalyzed dehydration of xylose and fructose over solid acid catalysts, mineral or ionic liquid catalysts [6–8]. Especially, furfural can be extracted directly from a variety of agricultural byproducts,

including corncobs, oat and wheat bran, sawdust, and rice husk [9–11], and bio-oil derived from fast pyrolysis of biomass [12]. Thus, the source of furfural is very extensive. Currently, furfural was used for the production of furfural resin and fine chemicals. It can be selectively hydrogenated to form furfuryl alcohol, 2-methylfuran or tetrahydro-2-furancarboxaldehyde [13,14] since furfural is a carbonyl compound containing unsaturated C=C bond and C=O bond. Furfural can also form longer carbon chain compounds by aldol condensation with ketone, which plays a key role in the production of higher alkanes ($C_8–C_{15}$) from biomass-derived carbohydrates such as xylose and fructose [2,4,15]. Currently, pentane could be used as pentane oil, or "bio-gasoline" when being added directly to fossil gasoline due to the similarity of its properties with gasoline. Thus, converting furfural to pentane through combination of hydrogenation and dehydration reactions would be a novel and meaningful approach.

Recently, Dumesic and his co-workers published a series of papers about production of alkanes from biomass-derived carbohydrates in aqueous-phase [2–5,16]. The hydrogenation catalysts used in these processes were supported noble metal catalysts, such as $Pt/SiO_2–Al_2O_3$ and $Pd/MgO–ZrO_2$ [2,5]. Crocker and co-workers reported that the liquid phase upgrading of a model bio-oil containing 4 wt.% furfural was investigated over a series of supported Pt catalysts [17]. These catalysts exhibited high catalytic activity and relatively suitable selectivity for production of alkanes. Well-known to us, nickel is an important catalyst for hydrogenation

and dehydrogenation, and its catalytic performance is comparable to noble metal catalyst [18,19]. Given low cost, mild reaction conditions and excellent catalytic activity of Ni-based catalyst, we loaded Ni on the commercial supports, such as γ-Al_2O_3 or SiO_2–Al_2O_3, and applied it to aqueous-phase catalytic hydrogenation/dehydration for alkanes production from furfural. It is desirable to use furfural for initial screening, while leaving the investigation of other biomass-derived carbohydrates and optimization of catalysts the subject of further research.

The main purpose of this study is to develop an approach of converting furfural to pentane over the inexpensive Ni-based bifunctional catalysts in water, which consists of repeated "one-pot" hydrogenation/dehydration reactions. The focus is on the effects of supporting material, reaction temperature, and nickel loading on conversion rate of furfural and selectivity for desired product.

2. Experimental section

2.1. Catalyst preparation

Ni/γ-Al_2O_3 catalysts were prepared by wet impregnating different amounts of γ-Al_2O_3 with Ni $(NO_3)_2 \cdot 6H_2O$ aqueous solutions. The solutions were evaporated and the residues were dried at 120 °C then calcined at 450 °C in the air. The catalysts contained 6, 10, 14 and 17 wt.% Ni, respectively. In the same way, the Ni/SiO_2–Al_2O_3 catalysts were prepared, which also contained 6, 10, 14 and 17 wt.% Ni, respectively. Supporting materials SiO_2–Al_2O_3 and γ-Al_2O_3 were commercial products, purchased from TRICI Science and Technology Development Corp. (Tianjin, China). Al_2O_3 content is 25 wt.% in the supporting material SiO_2–Al_2O_3. Catalysts were reduced at 450 °C before use.

2.2. Experimental equipment and method

All the aqueous-phase catalytic reactions of furfural were carried out in a 100 ml stainless autoclave equipped with an electromagnetic driven stirrer. The schematic diagram is shown in Fig. 1. For each run, 2.0 g catalyst, 40 ml water and 2.0 ml furfural were loaded in the autoclave. After displacing air, the H_2 pressure was raised to 3.0 MPa. The reaction temperature varied from 110 °C to 220 °C, reagents were vigorously stirred (800 rpm) in order to eliminate the limitation of diffusion. The cumulate gas efflux was measured when desired reaction temperature was achieved. Tail gas samples were collected in vacuum plastic bags for subsequent off-line gas chromatography (GC) analysis.

2.3. Product analysis and catalyst characterization

Product were analyzed by GC (Shimadzu GC2010 with a flame ionization detector (FID) and a DB-5 column, 30 m $\times$ 0.25 mm $\times$ 0.1 μm, N_2 as carrier gas), with alkanes (C_1–C_6) as the internal standard to confirm their components. The vaporization temperature was 58 °C, the detector temperature was 200 °C, and the oven temperature program ranged from 50 °C to 70 °C at the rate of 2 °C/min.

The BET surface area, External Surface Area, Average Pore Diameter and pore volume of catalysts were determined by N_2 isothermal (77 K) adsorption using Micrometrics ASAP-2010 automated system.

NH_3 temperature-programmed desorption (NH_3-TPD) studies were carried out in a quartz tube reactor with a thermal conductivity detector (TCD). Catalyst (100 mg) was pretreated in a flow of helium (30 ml/min) at 400 °C for 1 h to remove undesirable physisorbed species, and after cooling to 100 °C, ammonia adsorption was carried out. Physically adsorbed ammonia was removed by purging with helium at 100 °C for 2 h before the NH_3-TPD. All NH_3-TPD profiles were carried out by increasing the temperature from 100 to 600 °C with a rate of 10 °C/min and a helium flow rate of 30 ml/min.

H_2 temperature-programmed reduction (H_2-TPR) studies were carried out in a quartz tube reactor. Fifty milligrams of catalyst was pretreated in a flow of helium (30 ml/min) at 400 °C for 1 h to remove undesirable physisorbed species, and after cooling to 100 °C, the sample was heated in a flow of 5% H_2/95% N_2 (30 ml/min) from 100 to 800 °C at a heating rate of 10 °C/min. Hydrogen consumption was monitored by the change of thermal conductivity of the effluent gas stream.

TG studies of used catalysts were carried out under an air flow rate of 30 ml/min with analyzers by using 10–15 mg sample and a 10 °C/min temperature increasing.

3. Results and discussion

The mass balance of carbon estimated by sum of alkane products and unreacted furfural vs. fed furfural are about 90–96%.
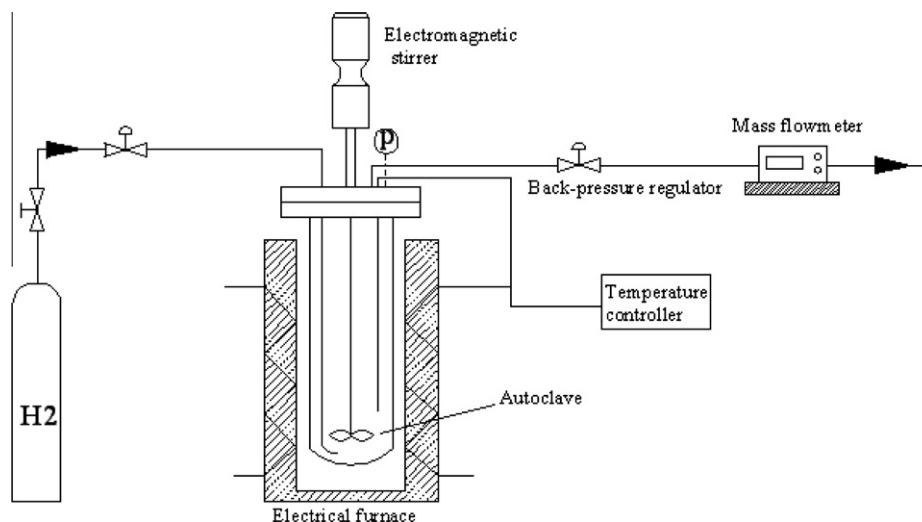

Fig. 1. Schematic diagram of experimental apparatus.