One-pot aqueous phase catalytic conversion of sorbitol to gasoline over nickel catalyst

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ABSTRACT

The carbon chain extension and hydrodeoxygenation steps play critical roles in the high-energy-density hydrocarbons production. In this paper, a systematic study had been carried out to investigate one-pot aqueous phase catalytic conversion of sorbitol to gasoline (STG) over bifunctional Ni-based catalysts. Characterization technologies of N_2 physisorption, X-ray diffraction (XRD), Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and NH_3 temperature-programmed desorption (NH_3-TPD) were used to study the textural properties, phase compositions, acid behavior and morphologies of the catalysts. The catalytic performances were tested in a fixed bed reactor. It was found that the physically mixed Ni/HZSM-5 and Ni/silica-gel (mesoporous SG) catalyst realized the carbon chain extension and exhibited excellent performances on hydrodeoxygenation (HDO) reaction (46.9% of gasoline (C5–C12) yield and 45.5% of C7–C12 hydrocarbons in the gasoline products). Especially, the temperature of STG (553–593 K) was lower obviously than that of the traditional methanol to gasoline (MTG) process (623–773 K). It provided a novel transformation of sorbitol to long-chain alkanes by one-pot process over the bifunctional catalyst (Ni@HZSM-5/SG), wherein hydrodeoxygenation, ketonization and aldol condensation steps were integrated.

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1. Introduction

Increasing issues on the environmental pollution and rapid consumption of fossil resources innovate strategies to explore sustainable production of fuels from renewable materials [1–4]. Biomass is currently the most abundant and inexpensive renewable alternative energy resources [5–8]. Biomass-derived sugar alcohol sorbitol has been reported as one of the ten platform compounds by the U.S. department of energy (DOE) [9,10]. In addition, it is easily obtained by hydrogenation of glucose or direct degradation/hydrogenation of cellulose, low thermal stability and natural hydrophility due to its high oxygen content with six hydroxyl groups [11,12].

Recently, many works (Table 1) on the conversion of the lingocellulosic biomass to gasoline-like products at lower temperature in comparison to other thermochemical technologies (e.g. pyrolysis or gasification) were reported [13–17], such as aqueous phase catalysis, which was a promising technology for direct conversion of sorbitol to liquid fuels [1,18–20]. Dumesic and co-workers

developed a process via the selective conversion of glucose and sorbitol firstly into monofunctional hydrocarbons, then further transferring to hydrocarbon fuel over heterogeneous catalysts [21]. The approach included three steps: (1) aqueous phase catalytic conversion of 60 wt% polyol solution to monofunctional compounds including furan, alcohol, ketone, and organic acids over the 10 wt% Pt–Re/C catalyst; (2) hydrogenation of these monofunctional compounds to alcohols over 5 wt% Ru/C at 5.5 MPa of H_2 pressure; (3) reforming of alcohols over the bifunctional $CuMg_{10}Al_7O_X$ catalyst to the C–C coupling of C4 to C6 ketones. Currently, the major challenge in the aqueous catalytic system is the development of the efficient conversion technologies and the hydrothermally stable catalysts. Several metal–acid bifunctional catalysts have been reported for catalytic conversion of polyol to hydrocarbons in gasoline-range, which included $Pt/SiO_2–Al_2O_3$ [22], $Pd/SiO_2–Al_2O_3$ [23], Pt/Nb_2O_5 [24] and $Pt/ZrO_2\_PO_x$ [25]. Vilcocq and co-workers reported that $Pt/ZrO_2–TiO_2–WO_x$ exhibited excellent performances with high sorbitol conversion and hydrocarbon fuels yield. However, the hydrocarbons product was usually light alkanes (C5–C6) over these catalysts [5,26]. Compared to the noble metal catalysts mentioned above, Ni/HZSM-5 was a cheap

bifunctional catalyst and there were many good works about its performances for liquid transformation into biofuel. Wherein, Gayubo and Yin reported its good selectivity for aromatics, alkanes, and olefins [27,28]. Our previous works concerned direct conversion of sorbitol into alkanes (C5, C6) [12,16,29].

The detailed process of MTG reaction was still not very clear, but generally believed that dimethyl ether was the key intermediate, which may undertake further dehydration into light olefins, and reforming into gasoline products (olefin, alkane, aromatic) [32–34]. Recently, we modified the Ni/HZSM-5 catalyst by silica gel (SG, amorphous structure, formed by Si–O tetrahedron, adsorption performance increasing as the hydrogen bonding with the Si–OH and Si–O–Si on surface) [32,35–37], and found that the modified catalyst showed high biomass sugar polyol conversion into gasoline (C5–C12 alkanes) by one-pot aqueous phase catalysis process. Interestingly, the produced oil products were predominantly straight-chain alkanes (pentane, hexane, heptane, octane, nonane, decane, undecance, odecane, etc.) and cyclic hydrocarbons, which are the important components of gasoline liquid fuels with high octane numbers [38–40]. Traditional C–C coupling processes include (1) ketonization, in which two carboxylic acid molecules react to form a linear ketone, CO_2 and water; (2) aldol-condensation/hydrogenation, in which two ketone or alcohol molecules react to form a heavier branched ketone [6]. But here, it was the first time to convert sorbitol directly to long-chain alkanes over bifunctional acid-metal catalysts (Ni@HZSM-5/SG). This one-pot process provided a simple and effective approach to integrate the hydrodeoxygenation, ketonization, and aldol condensation steps into a single fixed-bed reactor, and realized the carbon chain extension in the high-energy-density hydrocarbons production. The temperature (553–593 K) of aqueous phase catalytic reaction was lower than the temperature (623–773 K) of the traditional MTG reaction, which results in the improvement of conversion efficiency [39,41,42]. Therefore, the present approach provides an alternative approach for the production of gasoline from biomass via decreasing the dependence on fossil resources.

2. Experimental

2.1. Catalyst preparation

D-Sorbitol (CAS: 50-70-4) was purchased from Yuan-Ju biotechnology Reagent Co. Ltd. (Shanghai, China). HZSM-5 (Si/Al = 38, Nankai University catalyst Co., Ltd., Tianjin, China), and silica gel (SG, Qingdao Haiyang Co., Ltd., Shandong, China) were selected as support materials. All of the catalysts were synthesized by the method reported before [29,43]. Ni/HZSM-5 and Ni/SG were prepared by wet impregnation method with $Ni(NO_3)_2 \cdot 6H_2O$. The ratio of Ni loading on the catalysts was 10 wt%. Firstly, appropriate amount of carrier (HZSM-5 or SG) grains were impregnated with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ at 313 K for 12 h, followed by drying in air overnight, and then calcined at 823 K for 4 h. The Ni@HZSM-5/SG was prepared by mixing the Ni/HZSM-5 sample and Ni/SG sample (1:1 by mass). Subsequently, the mixture was grinded into slurry by adding appropriate amount of deionized

water. Then, the obtained slurry was stirred, dried and calcined under the conditions mentioned above. Prior to the reaction, all the catalysts were reduced under a flow of H_2 (50 ml/min) at 723 K for 4 h.

2.2. Catalyst testing

As shown in Fig. S1, aqueous catalytic reaction was carried out in a tubular stainless steel fixed-bed reactor (inner diameter of 10 mm, length of 350 mm) at 4 MPa. Before the reaction, 4 ml catalyst (≈1.5 g) was loaded in the constant temperature zone of the reactor with quartz sand and quartz wool as the filler materials on the top and bottom of the reactor, respectively. During reaction, 40 wt% sorbitol solution was pumped into the fixed-bed reactor at the flow rate of 0.05 ml/min by a high pressure liquid pump (HPLP). H_2 flow (150 ml/min) was purged into the reactor at the same time. The fixed reactor set-up kept H_2 pressure at 4 MPa with the use of pre-pressure controller and rear pressure, and operated in the co-current-flow of liquid and hydrogen from top to bottom. The reaction temperature varied from 533 K to 623 K.

As shown in Fig. S2, gaseous products were collected with a gasbag and analyzed by GC (TCD, FID, ±5%). Liquid products (oil phase and aqueous phase) were condensed and collected in an ice-water condensing tank. Due to spontaneous delamination, the oil phase would be extracted from the aqueous phase and the two phases weighted at Analytical Balance (±0.5%). The aqueous phase samples were further detected by HPLC with an error within ±2.27%. GC–MS (Thermo Trace GC Ultra with a PolarisQ ion trap mass spectrometer) equipped with a HP-5MS capillary column was applied to analyze the species in oil phase samples. An HPLC-MS (Agilent) equipped with an ion trap, was used to qualitatively identify the species in the aqueous phase sample. The total carbon content and C/H weight ratio in the liquid products were measured by a Vario EL **III** elemental analyzer (±0.2%).

2.3. Characterization

The crystalline structure of the catalysts were characterized by X-ray diffraction (XRD) (X Pert Pro MPD with Cu Kα (λ = 0.154) radiation, Philip) with scanning angle (2θ) ranging from 5° to 80°. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and SEM–EDS were used to study the textural properties, phase compositions, and morphologies of the catalysts. The textural properties of catalysts were determined by N_2 isothermal (77.35 K) adsorption on Mesoporous ASAP-2010 automated system. Surface area was calculated using the classical BET method, the micropore properties were evaluated by HK method and the mesoporous properties were evaluated by BJH method. NH_3 temperature-programmed desorption (NH$_3$-TPD) with a Micromeritics chemisorbs 2750 pulse chemisorption system was used to estimate the acidity (150 mg catalyst). The sample was firstly pre-treated by helium flow (30 cm^3 min^{-1}) at 573 K for 1 h, and then cooled to 303 K and ammonia-saturated in a stream of 10% NH$_3$/He flow (50 ml/min) for 1 h. The desorption of NH$_3$ was carried out in helium gas flow (30 cm^3 min^{-1}) by increasing the

Table 1
Typical low temperature catalysts for sugar alcohol conversion from biomass.

Catalyst	Feedstock	Conversion (%)	Alkane (selectivity, %)	P (MPa)	T (K)	Refs.
Pt–SiAl	Sorbitol	>90	C1–C6 (90)	3.48	498	[23]
NiSn	Sorbitol	>90	C1–C6 (32)	5.6	538	[30]
NiCuMo	Methyl palmitate	90	C15 (48)	1	573	[14]
Ni/HZSM-5	Sorbitol	67.1	C5–C6(98.7)	4	513	[31]
Ni@HZSM-5/SG	Sorbitol	>90	C1–C4(37.1) C5–C12(46.9)	4	573	This work