Aqueous phase reforming of sorbitol to bio-gasoline over Ni/HZSM-5 catalysts

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ABSTRACT

Liquid fuel such as bio-gasoline derived from biomass is widely recognized as a potential substitution for the diminishing fossil fuels due to its abundance of raw materials and lower greenhouse gas emissions. In this work, Ni/HZSM-5 catalysts were developed by incipient impregnation method and applied in the bio-gasoline production by aqueous phase reforming of sorbitol. The effects of reaction temperature, hydrogen pressure and calcination temperature of the catalysts on the catalytic performance were investigated. The activity test results showed that the catalyst calcined at 500 °C had the maximal activity with 47.6% of the bio-gasoline yield and 76.4% of the total selectivity of lighter alkanes (C6−C9) at 240 °C and 4.0 MPa. The catalysts were characterized by N2 physical adsorption, H2 temperature-programmed reduction (H2−TPR), H2 temperature-programmed desorption (H2−TPD), and infrared spectroscopy (IR) techniques. The characterization results revealed that the catalyst calcined at 500 °C can provide optimum surface area and pore volume for the reaction. Moreover, 100% of the reducibility of Ni species was detected on the surface of HZSM-5, following by more nickel active sites, which led to a visible increase in the yield of bio-gasoline.© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Diminishing fossil fuels would be substituted by renewable energy due to its grave environmental and rising price problems, especially the new liquid fuels from biomass resources [1,2]. Moreover, the production of liquid fuels is particularly attractive and promising because of its abundance of raw materials and lower greenhouse gas emissions comparing with those of the combustion of fossil fuels [3,4]. Significant efforts have been paid to develop cost-effective processes for biomass conversion to liquid fuels including the formation of methanol by Fischer−Tropsch synthesis of CO and H2 mixtures arising from biomass gasification, ethanol by fermentation of biomass, and bio-oils by pyrolysis or liquefaction of biomass [5−11]. Notably, a novel process called as aqueous phase reforming for the production of liquid alkanes (C6−C9) from sugar polyols such as sorbitol, a product of biomass-derived glucose hydrogenation [12,13], was initially proposed by Dumesic in 2004 [14]. In the process, hydroxyl groups of sorbitol were hydrogenated over a bifunctional metal−acid catalyst (e.g., Pt/SiO2−Al2O3) at 225 °C under the pressure of 3.96 MPa and then dehydrated into unsaturated species, following by successive hydrogenation and reforming into liquid alkanes (C6−C9) with the selectivity of 58−89%. In addition, an extra energy-intensive distillation for the products purification can be avoided due to the spontaneous separation of the alkanes from water, which can greatly improve the overall energy efficiency for liquid alkanes production, and thereby would result in industrial application in future biorefinery [15]. As a result, increasing attentions have been attracted on this process involved in the catalytic processing of biomass to liquid alkanes [16−21]. For instance, Li and Huber found that a closed-loop dehydration of sorbitol into C6 intermediate species was initially performed on the acidic centers and the cleavage of C=C bond of sorbitol into C5 polyols was present easily in the presence of Pt, accompanying by a large amount of decarburization. They also reported that bio-gasoline can be generated by aqueous phase hydrodeoxygenation of C6 and C5 sugar solutions over 4 wt% Pt/ZrP catalysts [19], Kirilin et al. [20] demonstrated that the aqueous phase reforming of sorbitol was quite complicated, and about 250 compounds were detected in the transformation intermediates of sorbitol by using gas chromatography combined with mass spectrometry. Furthermore, n-hexane and n-pentane were the main products of this process and no distinct increase in the octane number of gasoline was observed, which can be improved by zeolite HZSM-5 owing to its higher capacity of isomerization [22,23]. However, few researches have been reported about the zeolite supported Ni-based catalysts for aqueous phase hydrogenation of sorbitol to alkanes, particularly isoparaffins. Here, the Ni/HZSM-5 catalysts prepared by impregnation method were used to investigate the hydrogenation of sorbitol in the liquid phase. The effects of reaction temperature and hydrogen pressure on the catalytic performance of the catalyst were studied as well as the calcination temperature of the catalyst. The catalysts calcined at different temperatures were characterized

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by N2 physical adsorption, H2 temperature-programmed reduction (H2-TPR), H2 temperature-programmed desorption (H2-TPD), and infrared spectroscopy (IR) techniques to elucidate the effect of calcination temperature on aqueous phase reforming of sorbitol.

2. Experimental

2.1. Catalyst preparation

The catalyst used in this work was prepared by the incipient wetness impregnation method. Appropriate amounts of HZSM-5 grains (particle size of 60–80 mesh) was impregnated with an aqueous solution of nickel nitrate (Ni(NO3)2·6H2O) at room temperature for 12 h, followed by drying in air at 110 °C for 12 h, and then calcined at desirable temperatures such as 400 °C, 500 °C, 600 °C, or 700 °C, the corresponding catalysts were denoted as Cat-400, Cat-500, Cat-600, and Cat-700, respectively. The loading of Ni was a constant of 10 wt%. HZSM-5 (specific surface area of 320 m2/g, Si/Al atomic ratio of 38) was supplied by Nankai University catalyst Co., Ltd., China, and Ni(NO3)2·6H2O (AR, 99.9%) was bought from Tianjin Fucheng Reagents (Tianjin, China).

2.2. Catalytic activity test

The catalytic activity test was carried out in a batch-type high-pressure autoclave reactor with a capacity of 250 ml. Typically, 0.05 mol of sorbitol and 3.0 g of the catalyst were filled in the reactor with 150 ml of deionized water per run. Prior to activity test, a 0.32 mm3/2g, Si/Al atomic ratio of 38) was supplied by Tianjin Fucheng Reagents (Tianjin, China).

2.2. Catalytic activity test

The catalytic activity test was carried out in a batch-type high-pressure autoclave reactor with a capacity of 250 ml. Typically, 0.05 mol of sorbitol and 3.0 g of the catalyst were filled in the reactor with 150 ml of deionized water per run. Prior to activity test, the catalyst was reduced by a flow of H2 (30 ml/min) at 500 °C for 3 h. Moreover, H2 was displaced for three times so as to remove oxygen contained in the reactor, and then the reaction was performed at the desirable reaction temperature and hydrogen pressure for 1 h with the stirring speed of 200 r/min. The effluent products were displayed via a wet flow meter and were analyzed by a Shimazu GC-2010 gas chromatograph (SE-30 capillary column, 30 m × 0.32 mm × 0.32 μm) equipped with a flame ionization detector (FID). The alkane selectivity and bio-gasoline yield were measured according to the literature [14].

2.3. Catalyst characterization

Surface area and structural properties of the samples were measured by BET method on a TriStar 3020 instrument at −196 °C using N2 as adsorbent. Surface area was calculated using the classical BET method. The pore properties were evaluated by BJH method.

H2 temperature-programmed reduction (H2-TPR) was carried out on a self-made instrument. Typically, in order to remove the surface contaminants, 50 mg of the sample loaded in a quartz reactor was firstly pretreated at 350 °C in a pure N2 stream for 1 h. After cooling to room temperature, a flow of 5%H2/N2 (25 ml/min) was introduced into the sample, and the temperature was raised to 900 °C at a heating rate of 10 °C/min. The H2 consumption was monitored with a thermal conductivity detector (TCD) equipped with a 5 A molecular sieve to remove H2O from the effluent gas.

H2 temperature-programmed desorption (H2-TPD) was performed on the self-made instrument for H2-TPR. For per run, 200 mg of the sample loaded in a quartz reactor was initially reduced with H2 at 500 °C for 1 h, and then the reduced sample was treated in a flow of He (25 ml/min) for 30 min, followed by cooling to 50 °C. H2 adsorption was performed by switching the He flow to a pure H2 gas and then keeping at this temperature for 30 min. The temperature was raised from 50 to 800 °C at a heating rate of 10 °C/min. The amount of H2 desorption was measured by a thermal conductivity detector (TCD).

The infrared (IR) spectra were recorded on a Bruker TENSOR 27 FT-IR spectrometer with a resolution of 4 cm−1. Prior to analysis, the samples were pressed into a self-supported wafer at room temperature using KBr as the diluent.

3. Results and discussion

3.1. Aqueous phase reforming of sorbitol

Aqueous phase reforming gives an efficient route of the liquid alkanes production from biomass-derived sorbitol and the main reaction of hexane formation combined with sorbitol reforming into H2 and CO2 are given by Eqs. (1) and (2) below, which has been identified by Dumesic and co-workers over a bifunctional metal–acid catalyst (e.g., Pt or Pd/SiO2–Al2O3) [15,16]. Hydrogen is produced in the same reactor and would further supply H2 for the cleavage of C–C bonds or C–O bonds, which can be termed as C=C or C=O hydrogenolysis, respectively, wherein the former reaction is almost energetically neutral and the latter is highly exothermic [4]. Thus, the net reaction Eq. (3) is also exothermic and ca. 90% of the heating value of sorbitol reactant is saved in the hexane product. Additionally, when hydrogen was supplied externally as co-feed with sorbitol feedstock, the reaction of Eq. (2) would be inhibited without the formation of CO2 and therefore improving the selectivity of hexane by Eq. (1), which can also be varied by the reaction conditions, changing the catalyst composition, and the calcination process of the catalyst.

\[
\begin{align*}
\text{C}_6\text{O}_6\text{H}_{14} + 6\text{H}_2 & \rightarrow \text{C}_6\text{H}_{14} + 6\text{H}_2\text{O} & (1) \\
\text{C}_6\text{O}_6\text{H}_{14} + 6\text{H}_2\text{O} & \rightarrow 6\text{CO}_2 + 13\text{H}_2 & (2) \\
19/13\text{C}_6\text{O}_6\text{H}_{14} & \rightarrow \text{C}_6\text{H}_{14} + 36/13\text{CO}_2 + 42/13\text{H}_2\text{O} & (3)
\end{align*}
\]

3.2. Effect of reaction conditions on the catalytic performance

The effects of reaction conditions on the catalytic performance of the Ni/HZSM-5 catalyst calcined at 500 °C for sorbitol hydrogenation in the liquid phase are listed in Table 1. The bio-gasoline yield was found to increase rapidly with increasing reaction temperature. A lower bio-gasoline yield of 20.1% was achieved at the reaction temperature of 210 °C under the pressure of 4.0 MPa, whereas a higher value of 47.6% was obtained as the reaction temperature was further elevated to 240 °C. This implies that C=O hydrogenolysis in the sorbitol molecule can be easily performed at higher temperature, accompanying by a favorable desorption of effluents on the catalyst surface, similar phenomenon occurred in the aqueous phase reforming of xylitol reported in our previous study [24]. Meanwhile, the total selectivity of liquid alkanes (C5–C17) reached a value of 76.4%, of which the isohexane selectivity was 45.4%, suggesting that the isomerization of hexane can also be easily carried out at higher temperature. However, the bio-gasoline yield decreases as further increase in reaction temperature due to heavier cleavage of C–C bonds in the sorbitol molecule, which can be testified by the increasing amount of lighter alkanes (C1–C4) at 250 °C. In addition, the distribution of the product was affected closely by H2 pressure. The bio-gasoline yield was lower under H2 pressure of 3.0 MPa, which may be caused by the weak interaction between hydrogen and the sorbitol molecule or vaporization of the sorbitol solution at 240 °C. As mentioned above, appropriately enhanced hydrogen pressure can inhibit the formation of CO2 via water gas shift reaction and therefore a higher yield of bio-gasoline was present under H2 pressure of 4.0 MPa, while a decline in the bio-gasoline yield occurred under higher pressure (5.0 MPa) because of heavier C–C hydrogenolysis on metal sites.
Structural property of the catalyst is affected in a certain extent by different temperatures are summarized in Table 2. It is clear that the performance for aqueous phase reforming of sorbitol (left to right: 6 intervals are 25.6% over the catalyst calcined at 600 °C to 20.3%, accompanying by a visible drop in the selectivity of \( \text{C}_5 \) to 600°C, implying that \( \text{C}_5 \) decreased remarkably to 20.3%, whereas the bio-gasoline yield reached a maximal value of 47.6%, which may be caused by bigger surface area and more active sites over the Cat-500 catalyst. Meanwhile, the product of sorbitol hydrogenation was dominated by \( \text{i-C}_6 \text{H}_{14} \) with a higher selectivity of 45.4%. However, the bio-gasoline yield was found to be 25.6% over the catalyst calcined at 600 °C, whereas that of the catalyst calcined at 700 °C decreased remarkably to 20.3%, accompanying by a visible drop in the selectivity of \( \text{i-C}_6 \text{H}_{14} \) from 45.4% to 25.0%, wherein no significant change was observed on the selectivity of \( \text{n-C}_6 \text{H}_{14} \). In addition, the selectivity of \( \text{i-C}_6 \text{H}_{14} \) of the catalyst increased slightly as a function of calcination temperature in the range from 400 °C to 600 °C, and decreased dramatically at the calcination temperature as high as 700 °C, implying that \( \text{C}-\text{C} \) hydrogenolysis of sorbitol or the branched chain of \( \text{i-C}_6 \text{H}_{14} \) may occur easily on the catalyst calcined at higher temperature, which can be testified by the increasing selectivity of \( \text{n-C}_6 \text{H}_{12} \).

### 3.3. Effect of calcination temperatures on the catalytic performance

Fig. 1 shows the catalytic performance of the Ni/HZSM-5 catalysts calcined at different temperatures for sorbitol at 240 °C and 4.0 MPa. It can be seen that the catalytic performance of the catalyst was affected distinctly by calcination temperature. The bio-gasoline yield of 24.5% was obtained over the catalyst calcined at 400 °C, in which the total selectivity of liquid alkanes (\( \text{C}_5 \) to \( \text{C}_6 \)) was 61.0%. When calcination temperature of the catalyst was elevated to 500 °C, the bio-gasoline yield reached a maximum of 47.6%, which may be caused by bigger surface area and more active sites over the Cat-500 catalyst. Meanwhile, the product of sorbitol hydrogenation was dominated by \( \text{i-C}_6 \text{H}_{14} \) with a higher selectivity of 45.4%. However, the bio-gasoline yield was found to be 25.6% over the catalyst calcined at 600 °C, whereas that of the catalyst calcined at 700 °C decreased remarkably to 20.3%, accompanying by a visible drop in the selectivity of \( \text{i-C}_6 \text{H}_{14} \) from 45.4% to 25.0%, wherein no significant change was observed on the selectivity of \( \text{n-C}_6 \text{H}_{14} \). In addition, the selectivity of \( \text{i-C}_6 \text{H}_{14} \) of the catalyst increased slightly as a function of calcination temperature in the range from 400 °C to 600 °C, and decreased dramatically at the calcination temperature as high as 700 °C, implying that \( \text{C}-\text{C} \) hydrogenolysis of sorbitol or the branched chain of \( \text{i-C}_6 \text{H}_{14} \) may occur easily on the catalyst calcined at higher temperature, which can be testified by the increasing selectivity of \( \text{n-C}_6 \text{H}_{12} \).

### 3.4. \( \text{N}_2 \) physical adsorption results

Surface areas and structural properties of the catalysts calcined at different temperatures are summarized in Table 2. It is clear that the structural property of the catalyst is affected in a certain extent by calcination temperature ranging from 400 °C to 700 °C. Higher surface area of 267 m² g⁻¹ and pore volume of 0.20 cm³ g⁻¹ and the average pore diameter of 2.92 nm can be detected over the catalyst calcined at 500 °C, while those of the catalyst calcined at lower temperature (400 °C) or at higher temperature (600 or 700 °C) were both decreased slightly, implying that the nickel nitrate molecule may decompose completely at 500 °C on the surface of HZSM-5. Moreover, the micropore of the catalyst decreased obviously with increasing calcination temperature, wherein the micropore distribution descended from 14.5% to 8.0% as calcination temperature of the catalyst was elevated from 400 °C to 700 °C, whereas a reverse trend was apparent for macropores. The Cat-700 catalyst exhibited more macropores compared to other catalysts, suggesting a grown of the partial micropores into mesopores or macropores. Notably, the mesopore of the Cat-500 catalyst was a bit less than that of the Cat-400 catalyst, which may be due to the removal of the residues or decomposition products of nickel nitrate incompletely decomposed at 400 °C from the inner surface of the blocked pores. Generally, appropriate amount of macropores can promote the desorption of the products, following by the inhibition of some side reactions (e.g., the cleavage of lighter \( \text{C}_5 \) to \( \text{C}_6 \) alkanes), and therefore resulting in the elevation of the yield and selectivity of bio-gasoline.

### 3.5. \( \text{H}_2 \)-TPR/TPD results

The \( \text{H}_2 \)-TPR profiles of the Ni/HZSM-5 catalysts calcined at different temperatures are shown in Fig. 2. Two reduction peaks can be distinct over the Cat-400 catalyst, one at 442 °C ascribed to the reduction of superficial NiO, and the other at a higher temperature (539 °C) attributed to the reduction of bulk NiO [25]. The amount of \( \text{H}_2 \) consumption of the catalyst based on the peak areas in its TPR profile was measured to be 1.15 mmol g⁻¹. Thus, the reducibility of Ni species calculated from the amount of \( \text{H}_2 \) consumption for the catalyst was 86.1%. Interestingly, a shift to higher temperature of the reduction peak of NiO was observed over the Cat-500 catalyst, and the temperature of two reduction peaks was found to be round 503 and 583 °C, respectively, which was clearly higher than that in the Cat-400 catalyst, suggesting a stronger interaction between NiO and the support. Moreover, the catalyst showed the maximal amount of \( \text{H}_2 \) consumption of 1.34 mmol g⁻¹ cat with a whole reducibility of Ni species. In case of the Cat-600 catalyst, the temperature of two reduction peaks of NiO occurred at round 541 and 658 °C, the amount of \( \text{H}_2 \) consumption of the catalyst was measured to be 1.25 mmol g⁻¹ cat and the reducibility of Ni species was about 93.5%, indicating a bit sintering of Ni particles. Interestingly, the Cat-700 catalyst showed four reduction peaks, two of them at round 539 and 636 °C can be assigned to the reduction of superficial and bulk NiO, while those occurred at round 725 and 797 °C may be referred to the reduction of NiAl₂O₄ [26]. In addition, the amount of \( \text{H}_2 \) consumption based on the reduction of NiO over the Cat-700 catalyst was measured to be 0.61 mmol g⁻¹ cat and the reducibility of Ni species

### Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Yield (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{i-C}<em>6 \text{H}</em>{14} )</td>
<td>( \text{n-C}<em>6 \text{H}</em>{14} )</td>
</tr>
<tr>
<td>210</td>
<td>4.0</td>
<td>20.1</td>
<td>4.2</td>
</tr>
<tr>
<td>220</td>
<td>4.0</td>
<td>32.1</td>
<td>1.7</td>
</tr>
<tr>
<td>230</td>
<td>4.0</td>
<td>36.8</td>
<td>1.9</td>
</tr>
<tr>
<td>240</td>
<td>4.0</td>
<td>47.6</td>
<td>6.7</td>
</tr>
<tr>
<td>250</td>
<td>4.0</td>
<td>38.2</td>
<td>3.1</td>
</tr>
<tr>
<td>240</td>
<td>3.0</td>
<td>35.3</td>
<td>3.2</td>
</tr>
<tr>
<td>240</td>
<td>5.0</td>
<td>45.0</td>
<td>7.1</td>
</tr>
</tbody>
</table>

* The data was referred to the total yield of the alkanes ranging from \( \text{C}_5 \) to \( \text{C}_6 \).

** Others including the alkanes ranging from \( \text{C}_1 \) to \( \text{C}_4 \).
was about 45.5%. This indicates that Ni particles were sintered during the catalyst calcined at higher temperature.

The H\textsubscript{2}-TPD curves of the catalysts calcined at different temperatures are presented in Fig. 3. Three desorption peaks of hydrogen can be observed distinctly over these three catalysts, the peak at the temperature (round 392–463°C) can be attributed to the mild desorption of hydrogen on nickel active sites, and the peak at higher temperature (round 632–652°C) can be ascribed to the strong desorption of hydrogen on the metal surface, whereas the another peak at the temperature (round 711–746°C) can be associated with hydrogen strongly chemisorbed on the nickel surface, which has been confirmed to be hydrogen desorption of Ni\textsubscript{A}H species by Cui et al.\cite{27}, but it still needs to be proved that these Ni\textsubscript{A}H species have the promoting effect on the catalytic activity of sorbitol hydrogenation. In addition, the amount of hydrogen desorption over the catalyst calcined at 500°C was much higher than that of the catalyst calcined at lower temperature (400°C) or at higher temperature (600 or 700°C), indicating more nickel active sites on HZSM-5. It was also found that hydrogen desorption shifted to higher temperature as calcination temperature was elevated up to 700°C. This indicates that Ni particles can easily be sintered at higher temperature, which is consistent with the result of H\textsubscript{2}-TPR.

3.6. IR results

IR spectra of the catalysts calcined at different temperatures were collected at room temperature, as shown in Fig. 4. All the catalysts revealed the absorption bands at 503, 610, 664 and 936 cm\textsuperscript{-1}, which can be associated with the vibration of Si–O or Al–O groups of the HZSM-5 framework. Three additional absorption bands were found over the fresh Ni/HZSM-5 catalyst, the two bands at 711 and 1190 cm\textsuperscript{-1} can be assigned to the absorption of nitrate nickel molecule on HZSM-5, accompanying by a broadening of the band at 664 cm\textsuperscript{-1}, while the band at 1319 cm\textsuperscript{-1} can be attributed to the absorption of water arising from the crystal water in nitrate nickel or the inherent water in zeolite\cite{28,29}, which disappeared on the catalyst calcined at 400°C. Moreover, the band at 711 cm\textsuperscript{-1} vanished, and the broadening of the bands at 503, 664 and 936 cm\textsuperscript{-1} can be detected over the catalyst calcined at 400°C, suggesting that nitrate nickel decomposed to corresponding metal oxide and then interacted with zeolite or partly located in the zeolite lattices at 400°C. Interestingly, the relative intensities of the band at both 503 and 936 cm\textsuperscript{-1} decreased visibly, and the absorption band at 1190 cm\textsuperscript{-1} disappeared as calcination temperature further increased to 500°C, implying that nitrate nickel decomposed completely to NiO with small particle size. However, the intensity of

| Table 2: Surface area and structural properties of various catalysts. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Catalyst       | BET surface area (m\textsuperscript{2} g\textsuperscript{-1}) | Pore volume (cm\textsuperscript{3} g\textsuperscript{-1}) | Average pore diameter (nm) | Pore distribution (%) |
| HZSM-5         | 320             | 0.22            | 2.75            | 19.7            | 75.4            | 4.9          |
| Cat-400        | 261             | 0.18            | 2.81            | 14.5            | 81.5            | 4.0          |
| Cat-500        | 267             | 0.20            | 2.92            | 13.9            | 79.3            | 6.8          |
| Cat-600        | 261             | 0.19            | 2.89            | 9.1             | 84.3            | 6.6          |
| Cat-700        | 260             | 0.19            | 2.96            | 8.0             | 83.5            | 8.5          |

Fig. 2. H\textsubscript{2}-TPR profiles of the Ni/HZSM-5 catalysts calcined at different temperatures. (1) Cat-400; (2) Cat-500; (3) Cat-600; (4) Cat-700.

Fig. 3. H\textsubscript{2}-TPD curves of the Ni/HZSM-5 catalysts calcined at different temperatures. (1) Cat-400; (2) Cat-500; (3) Cat-600; (4) Cat-700.

Fig. 4. IR spectra of the Ni/HZSM-5 catalysts calcined at different temperatures. (1) Bare HZSM-5; (2) Ni/HZSM-5–110; (3) Cat-400; (4) Cat-500; (5) Cat-600; (6) Cat-700.
the bands at 503 and 936 cm\(^{-1}\) was found to increase distinctly when calcination temperature was elevated to 700 °C, which may be caused by the increasing size of NiO particles [30].

3.7. Economical analysis of bio-gasoline production from sorbitol

Hydrocarbon fuels derived from biomass are energy equivalent to those from petroleum, and the use of these renewable fuels can also favor the automobile industry to meet the increased standards of fuel economy imposed by governments [21]. Currently, per ton of bio-gasoline can be generated by about 2.1 ton of sorbitol feedstock, accompanying by 0.31 ton byproduct of lighter alkanes (C\(_1\)–C\(_4\)) usually used as liquefied petroleum gas (LPG) or for H\(_2\) production by steam reforming. The price of sorbitol and LPG in China is about 4000 RMB/ton and 5600 RMB/ton, respectively, thus, the cost of bio-gasoline production from sorbitol is calculated to be about 8100 RMB/ton plus the cost of energy consumption and devices, which is higher than that of commercial gasoline. In case that sorbitol feedstock is originated from lignocellulosic biomass by acid or enzymatic hydrolysis combined with hydrogenation, per ton of bio-gasoline can be produced from 8 to 9 tons of dried biomass material and thereby the cost would expect to decrease to 7000 RMB/ton. This is still competitive and promising under the large-scale industrial plant in comparison with the increasing price of conventional gasoline due to the diminishing fossil fuels. However, it should be noted that the Ni/HZSM-5 catalyst gradually deactivated as a function of reaction time due to the dealumination of HZSM-5 zeolite under the harsh hydrothermal condition (not shown), meanwhile, the formation of coke on the nickel centers and the leaching of nickel components into the liquid phase cannot be ignored during the reaction, which has been involved in our previous study [24]. Therefore, some measures are urgent to be taken into account for improving the catalyst stability in the future biorefinery.

4. Conclusions

The Ni/HZSM-5 catalyst was found to have high catalytic performance for the reforming of sorbitol to bio-gasoline in the liquid phase. There have obvious effects of reaction temperature and hydrogen pressure on the formation of bio-gasoline. A maximal value of 47.6% of the bio-gasoline yield and 76.4% of the total selectivity of light alkanes ranging from C\(_5\) to C\(_6\) over the Cat-500 catalyst were obtained at 240 °C and 4.0 MPa, wherein isoxeane was the dominated product with the highest selectivity of 45.4%. Furthermore, the temperature in the calcination step of the catalyst was also found to be a significant factor on the aqueous phase reforming of sorbitol. The optimum calcination temperature of the catalyst was confirmed to be 500 °C. The result of N\(_2\) physical absorption indicated that surface area and structural property of the catalyst were improved after calcination at 500 °C. The result of H\(_2\)–TPR revealed the catalyst calcined at 500 °C has the stronger interaction between Ni species and support with the highest H\(_2\) consumption of 1.34 mmol g\(^{-1}\) and 100% of the reducibility of Ni species. In addition, the results of H\(_2\)–TPD and IR displayed that nitrate nickel decomposed easily to small NiO particle over the catalyst calcined at 500 °C.

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