Hydrogenation and Ring-Opening of 5-Hydroxymethylfurfural to 1,2,6-hexanetriol over Pt/Al_2O_3 Catalyst

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Abstract:

1,2,6-Hexanetriol (1,2,6-HT) can act as building blocks for the polymer and is currently produced from petroleum, However, it also can be produced from lignocellulosic-derived biomass-5-Hydroxymethylfurfural (HMF) by ring-opening hydrogenation process. However, this process usually requires high pressure and temperature lead to great consumption of energy and catalyst. Therefore, we proposed a liquid-phase hydrogenation and ring-opening reaction to synthesize 1,2,6-HT under mild conditions. We attached noble metals to multiple kinds of support as a bifunctional catalyst, platinum on alumina oxide shows higher catalytic activity than other catalysts, the conversion of HMF was achieved at 100% and the yield of 1,2,6-HT was 40%.

Keywords: ring-opening hydrogenation, 1,2,6-Hexanetriol, mild condition.

1. Introduction

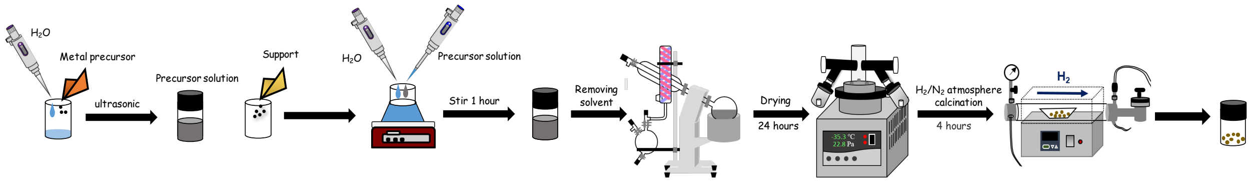
Our society relies heavily on petroleum to produce chemicals, it can lead to the decreasing fossil fuel reserves. However, renewable biomass is regarded as a promising alternative for fossil resources. Converting biomass feedstocks into bio-based chemicals are gradually being taken seriously. Among many biomass-derived chemicals, HMF is identified as an important platform molecular having aldehyde group, hydroxyl group and furan ring, which is generally produced from cellulose via hydrolysis or dehydration reaction, it can be further transformed into various value-added derivatives. 1,2,6-Hexanetriol (1,2,6-HT) is an important chemical which can be used as a precursor to produce 1,6-hexanediol. Currently, 1,2,6-HT generally produced from the complex hydrolysis and hydrogenation of oil-based acrolein dimer, in order to increase the sustainable application of diols, an alternative way to obtain 1,2,6-HT is converting HMF by the ring-opening hydrogenation process.

In the past, high-pressure hydrogen gas is normally used as the hydrogen source. In order to improve the reaction efficiency in milder condition, hydrogen-donating solvent, and chemical hydride can be provided another way for hydrogenation reaction. Chemical hydride such as sodium borohydride possesses high content of hydrogen capacity. On the other hand, catalyst which contains acid-based supports and noble metal is effective for the selective catalytic ring cleavage to obtain diols. In the past, many researchers (Yao[1] and Xiao[2]) have developed different catalysts for the ring opening of HMF. Unfortunately, such reactions usually require hydrogen gas as a hydrogen source, it is too dangerous to operate in high pressure. In addition, such processes were sometimes performed in toxic organic solvents or harsh conditions, it will lead to organic waste and high energy requirements.

2. Experimental (or Theoretical)

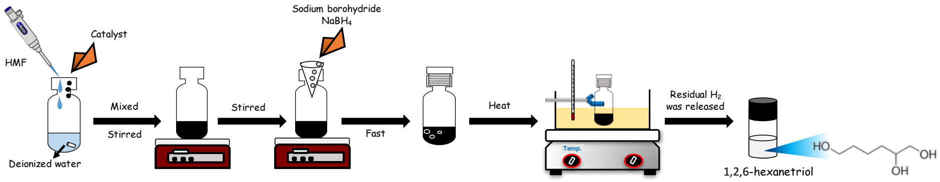
(1) Preparation of catalyst

Supporting noble metal on metal oxide catalyst was prepared by impregnation method. First, the precursor was dissolved in water. Then, we added metal oxide support, water, precursor solution into a vial stirring for 1 hour. After removing solvent by rotating evaporator, the powder was dried overnight and calcinated under H_2/N_2 atomosphere at 400°C for 4 hours to obtain catalyst.



(2) Hydrogenation and ring-opening of HMF

First, catalyst, HMF and water were charged into pressure tube. Second, $NaBH_4$ was quickly added into pressure tube and sealed tightly. When the reaction was finished, residual H_2 was released slowly. Finally, the product was analyzed by HPLC.



3. Results and discussion

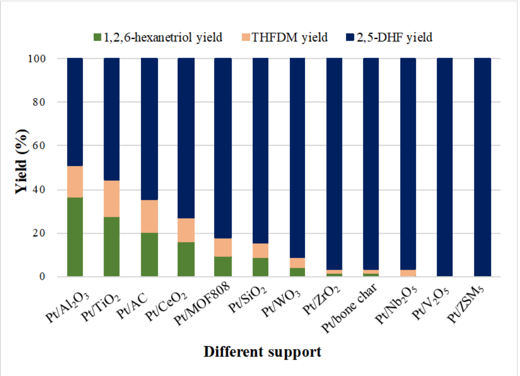


Figure 1. Effect of different support on the conversion of HMF

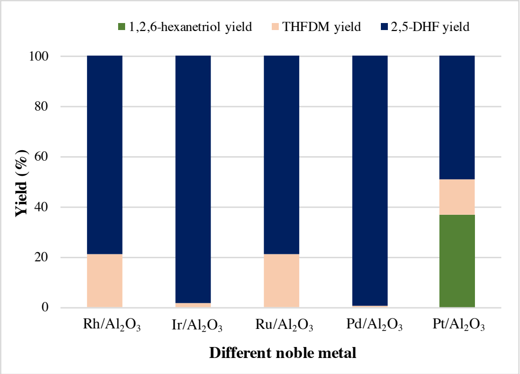


Figure 2. Effect of different noble metal on the conversion of HMF

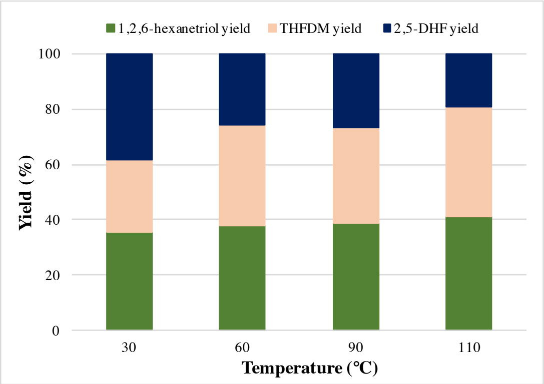


Figure 3. Effect of temperature on the conversion of HMF

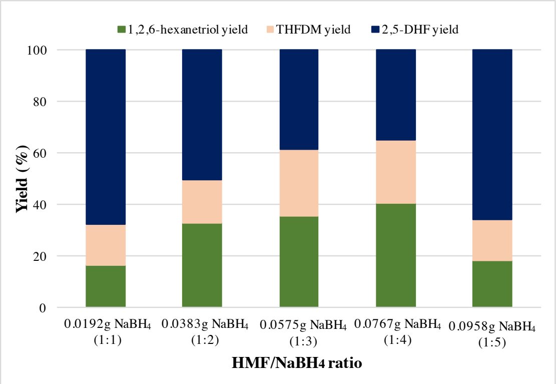


Figure 4. Effect of different HMF/NaBH$_4$ ratio on the conversion of HMF

The effect of reaction temperature on the hydrogenation of HMF. From the figure, we can found that in high temperature most of 2,5-DHF has converted to 1,2,6-hexanetriol and THFDM, but temperature at 30°C, still has many 2,5-DHF did not convert, As the temperature rise to 110 °C, although the conversion of 2,5-DHF was the highest, the yield of undesired THFDM also increase, it shows that high temperature may lead to hydrogenation of furan ring rather than ring-opening of furan ring. The amount of H_2 produced depended on the amount of $NaBH_4$ added. When the sodium borohydride added, HMF will quickly convert to 2,5-DHF, as the HMF: $NaBH_4$ ratio increased from 1:1 to 1:4, the yield of 1,2,6-hexanetriol rose sharply from 17% to 40%, but if further increasing the amount of $NaBH_4$, the yield of 1,2,6-hexanetriol declines, because the byproduct sodium metaborate precipitates, which blocks the active sites of the catalyst and reduces the activity of the catalyst.

4. Conclusions

In summary, we successfully set up a liquid-phase hydrogenation and ring opening of HMF over Pt/Al_2O_3 assisted with $NaBH_4$ under mild conditions without introducing any high-pressure H_2 gas. Under optimized conditions, we can produce 40% yield of 1,2,6-hexanetriol with the HMF: $NaBH_4$ ratio 1:4 at 30 °C and 24 hours.

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