

A MECHANISTIC STUDY OF GLYCEROL CONVERSION TO AROMATIC HYDROCARBONS OVER BIFUNCTIONAL METAL-SUPPORTED H- ZSM-5 CATALYSTS

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Abstract

The economics and sustainability of biodiesel manufacture can be improved by efficient utilization of its main by-product glycerol. In our prior study, a bifunctional catalyst (5 wt% Pd/H-ZSM-5) was designed for converting glycerol to hydrocarbon (GTH) fuels. In the present work, various bifunctional catalysts, with different Pd loadings and ZSM-5 acidity, were prepared, characterized and tested for GTH conversion. The active sites were determined and correlated with reaction rates for various steps, including glycerol dehydration to acrolein over acidic sites, acrolein hydrogenation to propanol over metal sites, propanol dehydration to propylene over acidic sites, and propylene dehydro-aromatization to aromatics over both metal and acidic sites. In addition to the mechanistic insights into GTH conversion, the present work provides the production of various valuable chemicals, such as acrolein, propanol and propylene, as well.

Keywords

glycerol to hydrocarbon (GTH), bifunctional catalyst, active sites, dehydration, hydrogenation.

Introduction

As biodiesel annual production has increased in the past two decades, a large amount of surplus crude glycerol has been generated. Utilization of glycerol, the primary byproduct (~10 wt%) of biodiesel production, is of importance to valorize biodiesel industry. Conversion of glycerol to hydrocarbon (GTH) fuels is among the promising options, which provides additional renewable energy besides biodiesel and contributes further to independence from fossil fuels. In our prior work [1], a bifunctional catalyst, 5% Pd/H-ZSM-5, was designed for GTH conversion. Under optimized conditions, ~90% glycerol conversion and ~60% yield of aromatic hydrocarbons were achieved. Based on experimental data over the same Pd/H-ZSM-5 catalyst, a lumped reaction net work and kinetic model were developed [2]. Using differential kinetic experiments

(glycerol conversion < 10%) over the temperature range 300–450 C, rate constants, reaction orders, and activation energies were obtained for each reaction step. The predicted values matched well with experimental data for glycerol conversion up to ~90%. In the present work, various bifunctional catalysts, with different Pd metal loadings and acidity of ZSM-5 support, were prepared, characterized and tested for GTH conversion. The active sites were determined and correlated with reaction rates for various steps in GTH, including glycerol dehydration to acrolein, acrolein hydrogenation to propanol, propanol dehydration to propylene, and propylene dehydro-aromatization to aromatics. The present work provides insight into GTH mechanism and the production method of various valuable

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chemicals, such as acrolein, propanol and propylene from glycerol.

Experimental

Materials, including metal precursor, ZSM-5 supports and calibration compounds, and catalyst preparation method were described in our prior works [1, 2]. NH_3 -TPD was used to measure acidity of catalysts, while H_2 - O_2 titration was employed to determine metal dispersion. Other characterization techniques, including BET, XRD, TEM, etc. were also carried out. The GTH tests were conducted in a continuous fixed-bed reactor system, described in our prior work [1,2].

Results and Discussion

Based on our prior work, Figure 1 shows the proposed reaction network for glycerol to hydrocarbons (GTH), including glycerol dehydration to acrolein (R1), acrolein hydrogenation to propanol (R2a), propanol dehydration to propylene (R2b), acrolein to aromatics (R3) and propylene dehydro-aromatization to aromatics (R4). Among these steps, the reaction rate of R3 is much lower than others, thus is not focus of the present work [2].

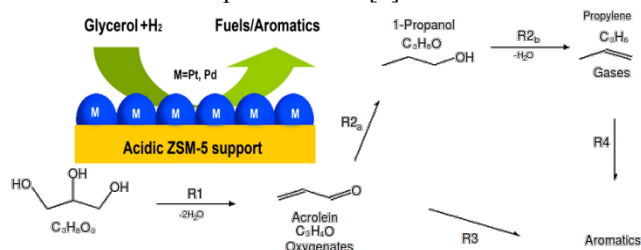


Figure 1. Reaction Network for Glycerol to Hydrocarbons (GTH)

Under differential operating conditions, three important parameters, including acidity of catalysts, Pd surface sites and H_2 partial pressure, were investigated and correlated with various steps, as shown in Figure 1.

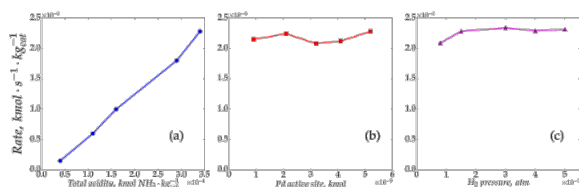


Figure 2. Correlation of R1 rate with acidity of catalysts, Pd sites and H_2 pressure.

Figure 2 shows correlations of these three parameters with the reaction rate of R1. It appears that glycerol dehydration (step R1) rate is linearly correlated with acidity of catalysts, while it is relatively insensitive with both Pd

sites and H_2 pressure. Similar results were also found for step R2b, propanol dehydration to propylene. Interestingly, for step R2a (acrolein hydrogenation), the opposite trend was observed, as shown in Figure 3. The rate of step R2a is linearly correlated with both Pd sites and H_2 pressure, indicating that hydrogenation occurs over surface Pd sites. For step R4 (propylene dehydro-aromatization), as shown in Figure 4, it was found that both acidity of catalysts and Pd sites promote the rate, while higher H_2 pressure gave lower rates, owing to the dehydrogenation feature of step R4.

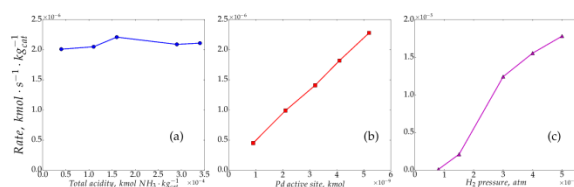


Figure 3. Correlation of R2a rate with acidity of catalysts, Pd sites and H_2 pressure.

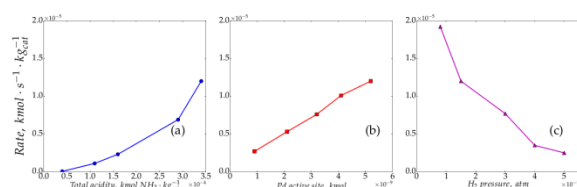


Figure 4. Correlation of R4 rate with acidity of catalysts, Pd sites and H_2 pressure.

Conclusions

The active sites were determined and correlated with reaction rates for various glycerol to hydrocarbon (GTH) steps, i.e. glycerol dehydration to acrolein over acidic sites, acrolein hydrogenation to propanol over metal sites, propanol dehydration to propylene over acidic sites, and propylene dehydro-aromatization to aromatics over both metal and acidic sites. The present work provides mechanistic insights into GTH conversion, as well as the production of various valuable chemicals, e.g. acrolein, propanol and propylene, etc.

Acknowledgments

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References

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