Design, Synthesis and Characterization of Novel Nano-metal Catalyst for Polyol Hydrogenolysis

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Introduction

The dwindling supplies of geological resources (fossil fuels) consisting of nonrenewable carbon and exponential growth in demand have left no choice to look for renewable resources for fuels and chemicals.

Cellulosic biomass and vegetable oils are considered as important renewable resources for converting to chemicals and fuels. While, the conversion of vegetable oils to bio-diesel has already been at advanced stage of commercialization, the long range sustainability of the technologies would largely depend on the competitive costs of the end product bio-diesel. Here, the large volume of glycerol produced as a co-product along with bio-diesel has particular significance, the utilization of which is most essential for the overall viability of the approach. Similarly, the sugars derived from the abundantly available biomass can be converted to polyhydroxy compounds, conversion of which to chemicals like glycols gives another opportunity to utilize renewable resources. Thus, "hydrogenolysis of polyols" deserves major attention in our efforts to arrive at new technologies. Several research groups have taken initiatives to explore this class of reaction [1]; however, there is a need for significant improvement in the performance of the process for polyol hydrogenolysis and selectivity to the desired products. We have extended the synthesis techniques developed earlier for nano-metal catalysts to design novel anchored nano-catalysts for hydrogenation of polyols [2]. In this presentation, the synthesis, characterization of the immobilized nano-catalysts and their application for hydrogenolysis of glycerol and cellobiose as model systems will be presented.

Materials and Methods

The nano-metal catalysts were immobilized on different supports using anchoring technique. The hydrogenolysis experiments were carried out in a 100 ml Parr autoclave and the liquid phase samples were analyzed using HPLC. The gas phase samples were analyzed at the end of the reaction using GC.

Results and Discussion

The anchored nano-metal catalysts were characterized by XRD, TEM, EDAX, CP-MAS-NMR to elucidate the structure of the synthesized material. A typical TEM image of the anchored Ru nano-catalyst is shown in Figure 1, which shows the uniform dispersion of the Ru nanoparticles on the solid support.

The immobilized nano-metal catalysts were tested for hydrogenolysis of glycerol and cellobiose (a dimmer of glucose). For comparison with conventional heterogeneous catalysts, the reactions were carried out at the identical conditions with commercial Pt, Pd, Ru and Rh catalysts. The influence of alkali promoter is also tested for the reaction. Ethylene glycol (EG), 1,2- and 1,3- PDO (propanediol) were the major products in all the cases. The typical reaction scheme for hydrogenolysis of glycerol and the experimental results with different catalysts (including anchored Ru nano-catalyst) and promoters are shown in Figure 2.

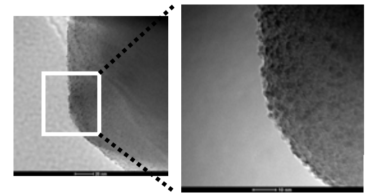

Figure 1. TEM image of the anchored Ru nano-catalyst

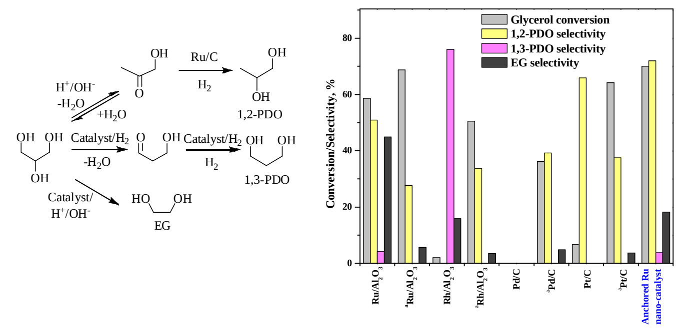

Figure 2. Reaction scheme and experimental results for hydrogenolysis of glycerol with different catalysts (a: NaOH promoter) (glycerol: 10% in H_2O; catalyst: 0.5g; 473K; 41 bar; 9h)

The results in Figure 2 show that the anchored Ru nano-catalysts give very good activity and selectivity to 1,2-PDO in glycerol hydrogenolysis. The obtained results are attributed to catalyst design and high metal dispersion characteristics. In the presentation, the other characterizations and catalytic experimental results will also be presented.

Significance

Deoxygenation of polyol deserves attention from the catalyst innovation, solvent engineering and process intensification point of view. In this presentation, our attempt to design and synthesize new catalytic materials based on the mechanistic understanding of hydrogenolysis reaction is addressed and novel supported nano-catalysts reported.

References

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