Selective conversion of concentrated sugars to 1,2-propylene glycol and ethylene glycol by using RuSn/AC catalysts

Jifeng Pang, Mingyuan Zheng*, Xinsheng Li, Yu Jiang, Yu Zhao, Aiqin Wang, Junhu Wang, Xiaodong Wang, Tao Zhang*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

*Corresponding author: E-mail: myzheng@dicp.ac.cn (Mingyuan Zheng); E-mail: taozhang@dicp.ac.cn (Tao Zhang)

Abstract: A series of RuSn/AC catalysts were synthesized for converting concentrated sugars to glycols of 1,2-propylene glycol (1,2-PG) and ethylene glycol (EG) in a semi-continuous reactor. Over the optimized 5%Ru3%Sn/AC catalyst, 25% and 26.9% yield of 1,2-PG and EG, respectively, was obtained with 10% glucose as a feedstock at 513 K for 10 min. The glycols productivity reached as high as 180 g L$^{-1}$ h$^{-1}$. Characterizations found that the highly dispersed SnO$_2$ was crucial to sugar isomerization and RuSn alloys played the role in retro-aldol condensation and hydrogenation.

Keywords: RuSn catalysts; concentrated sugars; 1,2-propylene glycol; ethylene glycol; hydrogenolysis.

1. Introduction (11-point boldface)

1,2-propylene glycol (1,2-PG) and ethylene glycol (EG) are important diols, which are widely used for synthesis of polyesters. On the other side, monosaccharides are regarded as key intermediates for glycols production, and the soluble sugars are convenient to be handled in terms of high concentration and continuous operation. Hence, it is very attractive to convert sugars to glycols [1].

Tungsten based catalysts were primarily used for glucose conversion. Over a binary catalyst of AMT and Ru/AC, the EG yield reached 60% at the glucose concentration of 5-10% [2]. For nickel promoted tungsten carbide catalysts, 66% EG yield at a volume productivity of nearly 300 gEG L$^{-1}$ h$^{-1}$ was achieved over the fed-batch system [3]. Recently, Tin based catalysts were found to be highly active for sugars conversion. The SnO$_x$ particles in Pt-SnO$_x$/Al$_2$O$_3$ catalysts promoted the conversion of cellulose to C$_2$ and C$_3$ compounds at a Sn/Pt atomic ratios larger than 2.1 [4]. Our recent study found that tin species played important roles in cellulose conversion to glycols over Ni-Sn catalysts [5]. Nevertheless, it is still a highly desirable to develop some novel catalysts for this reaction. Herein, a series of RuSn/AC catalysts were synthesized for efficiently conversion of monosaccharides to 1,2-PG and EG in a semi-continuous reactor. Structure of bimetallic catalts was characterized to illustrate the chemical state of catalysts, effects of tin loading and reaction parameters on glycols yield were investigated to optimize the glycols yield.

2. Experimental (or Theoretical)

RuSn/AC and SnO$_x$/AC catalysts were prepared by an incipient-wetness impregnation method. Catalytic conversion of sugars was carried out in a semi-continuous reaction system. Typically, certain amounts of catalysts and 20 mL of water were preloaded in a autoclave. The reactor was then flushed with 0.2 MPa hydrogen for 6 times and filled with 5 MPa hydrogen. The mixture was stirred at a rate of 800 rpm and heated to desired reaction temperatures. Finally, 20 mL of 10 wt% sugar solution was fed into the reactor by a high pressure pump and reacted for 10 min.

3. Results and discussion

![Image](image_url)

**Figure 1.** HRTEM imagines of 5%Ru/AC (a), 5%Ru2%Sn/AC (b), 5%Ru3%Sn/AC (c, e and f) and 5%Ru5%Sn/AC (d) catalysts. The insets in the corresponding images (a-d) show the particle size frequency distribution histograms.

To clarify the state of particles, the catalysts were characterized by HRTEM. As shown in Fig. 1 (a), Ru particles were highly dispersed with average diameter of ca. 1.7 nm on the 5%Ru/AC catalyst. After introducing 2% and 3% of tin, the average diameter of particles gradually increased and reached 2.7 nm and 3.3 nm, respectively (Fig. 1, b and c). In contrast, some particles with diameters larger than 6 nm were observed apart from the particles of 3-4 nm over the 5%Ru5%Sn/AC catalyst (Fig. 1, d). The lattice spacings of typical particles (Fig. 1, e and f) indicated that the Ru-Sn alloy partially formed between the metallic Ru and tin species on the 5%Ru3%Sn/AC catalysts.
Quasi in-situ XPS characterizations were conducted to disclose the state of catalysts under reduction conditions. As shown in Fig. 2 A, RuO$_2$ was transformed to metallic Ru after reduction. Comparing the reduction temperature with the reaction conditions for sugars conversion (523 K vs. 518 K), one can propose that the Ru should be at metallic state under reaction conditions. For the chemical state of tin, 13% of tin was metallic in the as-prepared catalysts before in-situ reduction, which was increased to 77% after reduction. The high percent of metallic tin after in-situ reduction demonstrates that most tin oxide species co-existed with Ru particles over the 5%Ru3%Sn/AC catalyst, which facilitated the hydrogen spillover from Ru particles to tin oxides, and resulted in the RuSn alloy.

In order to clarify the coordination environment and valence state of tin species, the 5%Ru3%Sn/AC catalyst was characterized with $^{119}$Sn Mössbauer spectroscopy. As shown in Fig. 3, the doublet with an IS value of 0.2 was attributed to the Sn$^{4+}$, and the singlet with IS value of 2.4 was attributed to the Sn$^0$ in the RuSn alloy. The quadrupole splitting value for Sn$^{4+}$ is much larger than that of bulk SnO$_2$ (0.75 vs. 0.58 mm/s), suggesting that the tin oxides on RuSn/AC catalysts had a low symmetric geometry.

Glucose was used for catalytic evaluation. As shown in Fig. 4, the tin loading on the catalyst greatly affected the product distributions. Over the 5%Ru/AC catalyst, the primary product is hexitols at a yield of 49%, with 9% overall yield of 1,2-PG, EG and glycerol. The introduction of tin significantly decreased the hexitols yield to 4.4% at 3% tin loading. In contrast, 1,2-PG and EG yields increased sharply, up to 25% and 26.9%, respectively, with 67% overall yield of glycols. Further increasing the tin loading to 6% caused a significant decrease in the yield of glycols (down to 26.6%) and notable amount of humins formation.

4. Conclusions

Tin modified Ru/AC catalysts were synthesized for converting sugars to glycols. The tin loading greatly affected the structure of catalyst. Under optimized tin loading of 3%, 23% of tin was present as tin oxides with 77% tin exist as RuSn alloy, which showed balanced ability for glucose isomerization, retro-aldol condensation and hydrogenation reactions. Over which, the yield of 1,2-PG and EG reached 25% and 26.9%, respectively, with overall glycols yield of 67% for glucose conversion at 513 K for 10 min. The glycols productivity reached nearly 180 g L$^{-1}$ h$^{-1}$. The highly dispersed SnO$_2$ promotes the glucose isomerization, and the produced fructose along with unreacted glucose are transformed to glycols of EG and 1,2-PG over the RuSn alloy via retro-aldol condensation and hydrogenation reactions.

References