

Editorial

# New Trends in Catalytic Conversion of Glycerol

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Glycerol is the core byproduct in the production of biodiesel. In recent years, with the booming of the biodiesel industry, a huge amount of glycerol has been generated. Value-added applications of glycerol as a low-cost raw material for chemicals and fuels have attracted increasing attention. Due to the highly functionalized molecular structure of glycerol, it can be catalytically converted into many high-value chemicals/fuels, including citric acid, lactic acid, 1,3-dihydroxyacetone, 1,3-propanediol, 1,2-propanediol, dichloro-2-propanol, acrolein, solketal, hydrogen, ethanol, etc. To realize efficient and cost-effective production of these chemicals/fuels from glycerol, the development of proper heterogeneous catalysts or biocatalysts, and catalytic processes is essential. According to the target products, catalytic strategies for glycerol conversion can be classified into oxidation, dehydration, acetylation, esterification, reforming, reduction, etherification, ammoxidation, acetalization, and gasification. Utilization of glycerol is an emerging field with significant demand for research in glycerol conversion via heterogeneous and homogeneous catalysis.

This Special Issue on “Catalytic Conversion of Glycerol” shows recent advances in the development of catalytic systems for the utilization of glycerol. Besides catalysts, the roles of additives, effects of reaction conditions, and reaction mechanism were also covered.

This Special Issue includes ten articles and three reviews. Lee and co-workers focus on the catalytic etherification of glycerol [1–3]. In one of their research works, alkali acetate salts such as NaOAc and KOAc were used as catalysts, and weakly acidic alkali metal-based inorganic salts (NaHSO<sub>4</sub> and KHSO<sub>4</sub>) were used as additives for the conversion of glycerol to diglycerol (DG) and triglycerol (TG). The additives can act as inhibitors to moderate the activity of the catalysts. By moderating the activity, the formation of higher oligomers was depressed, leading to the increase of selectivity of DG and TG [1]. Based on this research, the authors further developed heterogeneous catalysts for this reaction. Using X-type zeolite as a heterogeneous catalyst and NaHSO<sub>4</sub> or KHSO<sub>4</sub> as an additive, etherification of glycerol to DG and TG was carried out. In this catalytic system, the additive could also moderate the activity of the zeolite and increase the selectivity of DG and TG. Interestingly, in the presence of the additives which could depress the formation of higher oligomers, the recyclability of the catalyst was much enhanced [2]. Lee and co-workers also applied the alkali metal cation (Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup>) containing X-type zeolites (MX) to catalyze the etherification of glycerol [3]. It was found that the catalytic activity showed the following trend: KX > LiX > NaX, but the trend of selectivity of DG and TG was XZ-Li > XZ-Na > XZ-K. Overall, XZ-Li demonstrated the best catalytic performance among the catalysts tested. After optimizing the reaction conditions, 89.6% glycerol conversion, 61.2% DG yield, and 21.2% TG yield were obtained over the LiX catalyst [3]. Hydrogenolysis is another important strategy for the conversion of glycerol to high-value chemicals. Ng, et al. applied a Pd-promoted Cu/MgO/Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrogenolysis of glycerol to 1,2-propanediol (1,2-PD) using in situ hydrogen source provided by the reforming of methanol [4]. The introduction of Pd could improve the glycerol conversion and 1,2-PD selectivity by enhancing the hydrogenation of acetol. Meanwhile, the study proved



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that glycerol concentration influenced the 1,2-PD selectivity greatly, and higher glycerol concentration led to lower 1,2-PD selectivity [4].

Production of methyl lactate from glycerol was studied by Xu et al. using an Au-CuO/Sn-Beta catalyst [5]. Au-CuO provided the active sites for the oxidation of glycerol to 1,3-dihydroxyacetone (DHA) and Sn-Beta acted as the Lewis acid to catalyze the conversion of DHA to methyl lactate. The synergistic effect between the two active sites realized the highly efficient production of methyl lactate from glycerol. After the reaction at 90 °C for 6 h, 59% methyl lactate yield was obtained [5]. Castanheiro realized the acetalization of glycerol with citral by using KIT-6-supported tungstophosphoric acid as a catalyst [6]. Increasing the amount of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> on KIT-6 led to an increase in glycerol conversion. At the optimized reaction conditions, 89% glycerol conversion was observed. Furthermore, this catalyst was stable [6].

Nowadays, hydrogen has become a valuable energy resource. Reforming glycerol is an attractive strategy for the production of hydrogen. In the paper by Ibrahim et al., kinetics for crude glycerol autothermal reforming was investigated at a steam/carbon ration of 2.6 and an oxygen/carbon ratio of 0.125 using Ni/CeZrCa as a catalyst [7]. The Eley-Rideal model was hypothesized and proved to be the most suitable for the description of the reaction rate. In this model, the reaction between the adsorbed intermediate and steam was the rate-limiting step. The power rate law model was found to be the most suitable for total oxidation, and the Eley-Rideal-type mechanism was the best for the description of the CO<sub>2</sub> methanation reaction [7]. Ayastuy and co-workers studied the aqueous-phase reforming of glycerol over NiAl catalyst [8]. Two different template removal methods were used in the synthesis of the catalysts. The textural, acid-base, structural, and compositional properties were characterized and discussed. The prepared catalysts could realize the aqueous-phase reforming of glycerol at 235 °C and 35 bar. Meanwhile, physical-chemical properties and catalytic performance of the spent catalysts were also characterized and tested. It proved that nickel was oxidized in the liquid phase reforming [8]. Besides reforming, glycerol can also act as a green hydrogen source in catalytic transfer hydrogenation reactions. Bingwa and co-workers applied perovskite types metal oxides (SnO<sub>2</sub>, LaFeO<sub>3</sub>, and LaSnO<sub>3</sub>) as catalysts and glycerol as the hydrogen source for the hydrogenation of cinnamaldehyde [9]. These catalysts showed high catalytic activity, affording 99% cinnamaldehyde conversion. In addition, the authors found that these catalysts also showed activity for the etherification of glycerol. Competitive surface catalytic reactions related to cinnamaldehyde and glycerol were proposed by the authors. The transition metal cations provided the binding sites for the cinnamaldehyde and the sacrificial glycerol.

Gull and co-workers reported the utilization of glycerol for the synthesis of glycerol phosphate esters which could be used as a model molecule to study the origin and evolution of life [10]. Using various rock samples, salts, and minerals as catalysts, glycerol-1-phosphate, glycerol-2-phosphate, cyclic glycerol-monophosphate, and various diphosphate esters were prepared successfully. The decomposition of the glycerol phosphate ester was also studied. It was proved that these esters decomposed quickly under mild heating conditions.

In the review by Dalai et al., various utilization strategies for glycerol including carboxylation, oxidation, etherification, hydrogenolysis, esterification, and dehydration were introduced [11]. To provide more guidance information for the efficient production of valuable chemicals from glycerol, the effects of many factors including the type of acidic or basic sites and the supports related to catalysts, reaction pathways, and operating parameters were summarized and discussed. Furthermore, the market and applications of glycerol, its derivative products, and related prospects were discussed in this review [11]. Palanychamy and co-workers summarized the research progress in glycerol etherification [12]. The glycerol etherification mechanisms in different solvent systems including alcohol solvent, olefin solvent, and solvent-free were investigated. Product distributions in different solvent systems were summarized systematically. In this review, the authors believed that base-catalyzed glycerol etherification via a solvent-free reaction route is a desired way to improve glycerol conversion and product selectivity [12]. In the review

by Xu et al., research advances in the production of green hydrogen and valuable chemicals from glycerol were summarized and discussed [13]. The performance of various catalytic systems in glycerol reforming, dehydration, oxidation, hydrogenolysis, and so on was covered in this review. The authors pointed out that the catalyst deactivation must be addressed in future research. It was suggested that the design of some novel reactor configurations could be a route to address the catalyst deactivation issue [13].

In summary, the manuscripts published in this Special Issue cover various catalytic strategies for the production of fuels and valuable chemicals from glycerol. We would like to thank all the authors for their valuable contributions to the development of new catalytic systems for the conversion of glycerol. We are honored to be the Guest Editors of this Special Issue, and grateful to all the staff of the *Catalysts* Editorial Office.

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