

BIOMASS TRANSFORMATION WITH SOLID ACID AND BASE CATALYSTS IN NEAR-CRITICAL AND SUPERCRITICAL WATER

Masaru Watanabe*, Toru Iida, Yuichi Aizawa, Hiroshi Inomata
07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan
Email: meijin@scf.che.tohoku.ac.jp, Fax: +81-22-217-7282

In this study, we examined the effects of some metal oxide catalysts for biomass (glucose, glycerol, and vegetable oil) conversion in near- and supercritical water, using batch reactors. For glucose reactions, reaction temperatures ranged from 473 to 723 K. Above 573 K, glucose was converted more than 10 % conversion within a heat-up time. However, gasification *via* retro-aldol condensation mainly proceeded above 623 K regardless with and without catalyst. At lower temperature (473 K), dehydrogenation of glucose occurred and some metal oxides (TiO₂) enhanced the dehydrogenation. For glycerol and vegetable oil conversion, ZrO₂ was possibly act as a base catalyst.

INTRODUCTION

Recently, near- and supercritical water (NCW and SCW) has been known as a green chemical environment for some organic reactions because they can proceed without any catalyst [1-18]. However, some reactions, such as dehydration of small alcohols [15-18] and decarboxylation of acetic acid [19], requires addition of acid (such as H₂SO₄) or base (such as NaOH) for the increase of the selectivity of the reactions. However, homogeneous acids and bases would be normally used for pH controlling of water, the acid and base have a negative impact for the inner wall of a reactor and the global environment.

One of the possibilities for green-chemical pH control technique is to use a solid and base catalyst in SCW. The authors show that HCHO reaction can be controlled by CeO₂, MoO₃, TiO₂, and ZrO₂ [20]-[22]. Furthermore, we confirmed the acidity or basicity of metal oxides for various chemicals in SCW. The other researchers show that MoO₃ is an acid catalyst for hydration of propylene [23]. These results suggest that a metal oxide can work as an acid or a base catalyst for the organic reactions in SCW, instead of a homogeneous acid or alkali.

In this study, we examined the catalytic acidic and basic effects for biomass conversion in SCW. We employed glucose, glycerol, and vegetable oil as biomass. Through the study, the possibility of new process of biomass transformation with metal oxide catalyst and SCW (and NCW) would be discussed.

EXPERIMENTAL

Metal oxides were purchased from Merck (CeO₂) or Wako Pure Chemicals Co. Zirconia catalyst (ZrO₂) was prepared by calcination of zirconium hydroxide at 673 K for 3 h. Zirconium hydroxide (ZrO₂·xH₂O) was purchased from Nakarai Tesque Inc. Glucose was from Aldrich. Glycerol (+ 99 % of purity) and stearic acid (+ 95 % of purity) were purchased from Wako Pure Chemicals Co. and used without further purification. Vegetable oil was commercial salad oil. Tetrahydrofuran (THF) with a stabilizer was also obtained from Wako Pure Chemicals Co. Pure water, that was distilled after deionization, was supplied by a water distillation apparatus (Yamato Co., model WG-220).

The reaction was carried out by use of a SS 316 stainless steel tube bomb reactor with an inner volume of 6 cm³. The loaded amount of sample was 0.1 g, and the loaded amount of water was 1.0 g. Metal oxide catalyst was introduced with 0.3 g. After loading the sample, water, and the catalyst, argon gas (Ar) was pressurized at 1 MPa after purging of air in the reactor. Some experiments without water and catalyst were also conducted for the comparison. The reactor was submerged in a fluidized sand bath (Takabayashi Riko Co., model TK-3) whose temperature was controlled to remain at the reaction temperature. The reaction times ranged from 15 sec to 60 min. The reactor was taken out of the bath and rapidly quenched in a water bath after a given reaction time. After the reactor reached room temperature, the stop valve connected to the reactor was joined to a syringe that was equipped with gas samplers to collect the produced gas and measure its volume. The reactor was opened after the sampling or displacement of the gaseous products and washed with water or THF to recover the liquid products and solid including the catalyst. The recovered solution that had the catalyst was filtered with a membrane to separate into the liquid products and the catalyst.

The identification and quantification of the gaseous products were accomplished by GC-TCD (Shimadzu, model GC-7A, and Hitachi, model GC163). An external standard was added to each water solution for analytical purposes. Identification and quantification of liquid products in the THF solution were conducted by GC-MS (JEOL, model JMS-700) and GC-FID (Hewlett Packard, model 6890). In the case of water solution, we evaluated the amount of carbon atom in the solution by use of TOC (Shimadzu, TOC-5000). Conversion of the reactant was evaluated from the amount of reactant recovered and that loaded. The metal oxide catalysts before and after the reaction were analyzed by an X-ray diffractometer (Rigaku, model MiniFlex) with Cu Ka radiation.

RESULTS AND DISCUSSION

Glucose conversion

For glucose conversion, the products, which were qualified and quantified, were H₂, CO, CO₂, C₁ ~ C₄ hydrocarbons, 1,6-anhydroglucose, 5-hydroxymethylfurfural (5HMF), and furfural. The value of TOC (total organic carbon in the recovered water) was evaluated. The yields of short hydrocarbons were negligibly small for all the experimental conditions. The lack of mass balance (= 100 - (TOC + gaseous carbon (CO, CO₂, and hydrocarbons))) was possibly due to the water insoluble products which were not measured.

First of all, the reaction within heat-up time was studied. **Figure 1** shows the heating profile inside the reactor (sand bath temperature were 473, 573, and 673 K). For all the cases, the heat-up time to the desired temperature was about 60 sec.

Figure 2 shows the gaseous products of glucose reaction in NCW and SCW within heat-up time (namely 60 sec of reaction time). As shown in Fig. 2, the gasification was enhanced above 623 K. At 773 K, 10 % of glucose gasification was reached within 60 sec in the absence of catalyst. Furthermore, the ratio of CO to CO₂ increased with increasing temperature. This indicates that the gasification proceeded via retro-aldol condensation (namely via formation of aldehydes) because the thermal decomposition of aldehydes mainly forms CO.

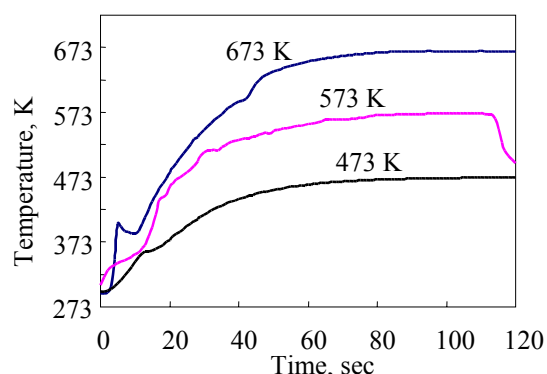


Figure 1 Temperature profile inside the reactor

Figure 3 is the results about liquid products of glucose reaction in NCW and SCW within heat-up time. Even at 573 K, 20 % of glucose converted into dehydrogenated products within 60 sec. By processing the gasification (above 623 K), the liquid products drastically decreased.

Based on the above fundamental studies, we elucidate the effect of metal oxides on glucose reaction in NCW at 473 K, mainly.

By adding the TiO_2 , the yield of dehydrogenation products such as 5-HMF were enhanced. On the other hand, ZrO_2 promoted isomerization of glucose into fructose. These indicate that TiO_2 has a weak acidity, while ZrO_2 a weak basicity for glucose reaction in NCW (473 K).

Glycerol conversion

Bühler et al. [24] reported that glycerol reaction proceeds via ionic and radical reaction depending on the reaction conditions. This probably implies that the reaction of glycerol could be controlled by acidity and basicity of metal oxides. Therefore, we examined the glycerol reaction with metal oxides at 673 K and 30 min. As a result, ZrO_2 enhanced the glycerol conversion significantly. Now we are studying the glycerol reaction with various metal oxides by focusing on the products in more detail.

Vegetable oil conversion

Vegetable oil is hydrolyzed rapidly in NCW even at 573 K [25]. For recovering hydrocarbon from vegetable oil, decarboxylation of free fatty acid is a key reaction. We confirmed that a long chain free fatty acid (stearic acid was employed in this study) was stable in SCW even at 673 K. Thus, some metal oxide catalysts were attempted to enhance the decarboxylation. **Figure 4** shows the effect of ZrO_2 on stearic acid

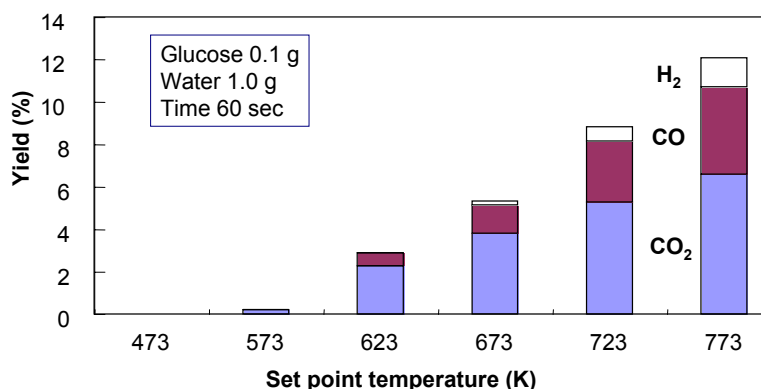


Figure 2 Gaseous products of glucose reaction in NCW and SCW within heat-up time

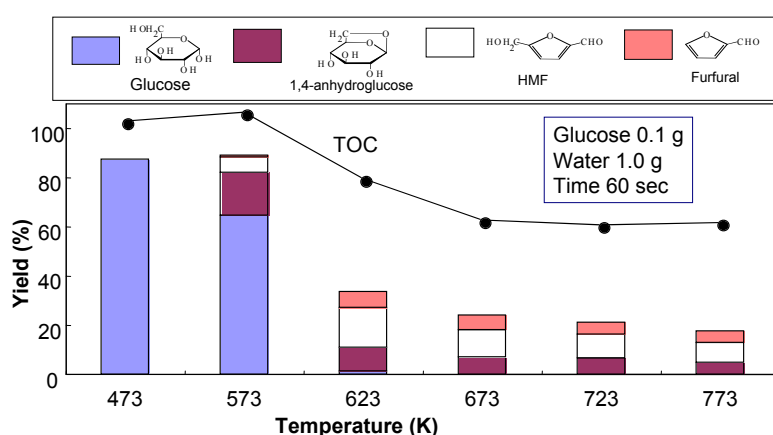


Figure 3 Liquid products of glucose reaction in NCW and SCW within heat-up time

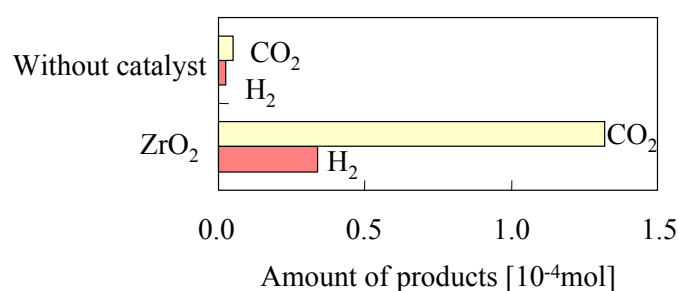


Figure 4 Effect of ZrO_2 on decarboxylation of stearic acid in SCW at 673 K (30 min)

decarboxylation in SCW at 673 K. In the presence of ZrO_2 , decarboxylation was greatly enhanced as shown in Fig. 4. The similar effect was found on the vegetable oil conversion. In near future, we will treat much amount of vegetable oil by the technique and elucidate the character as diesel fuel.

CONCLUSION

Isomerization of glucose, glycerol conversion, and decarboxylation of vegetable oil were enhanced by ZrO_2 catalyst in NCW and SCW. Thus, ZrO_2 is solid base catalyst for the biomass conversion in NCW and SCW. On the other hand, dehydrogenation of glucose was promoted by TiO_2 . TiO_2 is probably solid acid catalyst in NCW and SCW.

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