

Catalytic conversion of glucose and cellobiose into ethylene glycol over various tungsten-based catalysts

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Abstract: Glucose and cellobiose were used as model compounds to investigate the effect of retro-aldol condensation and hydrogenation rates on the product distribution of cellulose conversion. It was shown that the product distribution obtained over the physical mixture of Ni/SBA-15 and WO₃/SBA-15 in the glucose and cellobiose conversions were different from that attained on the Ni-WO₃/SBA-15 prepared by the co-impregnation method. The ethylene glycol (EG) yield depended on the structures of tungstic compounds, and it increased in the order of WO₃ < WO₃/SBA-15 < (NH₄)₆W₇O₂₄·6H₂O (AMT), while the particle sizes of them decreased in such an order. Regardless of the types of tungstic compounds, the EG yield obtained in the glucose conversion is lower than that attained in the cellobiose conversion at the same amount of catalyst.

Keywords: glucose; cellobiose; hydrogenolysis; tungsten-based catalysts; ethylene glycol

Lignocelluloses, one of the major clean energy resources, has been considered to be a potential feedstock alternative to fossil resource for production of clean energy and renewable chemicals because of increasing concerns about the shortage of fossil fuels and the global warming as a result of emission of great amounts of CO₂^[1,2]. Up to date, many routes have been developed for the sustainable production of liquid fuels and chemicals from lignocelluloses^[3–12]. Among the proposed routes, one-pot transformation of cellulose into ethylene glycol (EG) has attracted considerable attention because EG is an important commodity chemical widely applied in the synthesis of polyesters, antifreeze and cosmetics, etc^[5,13].

In 2008, Ji et al^[5] reported that nickel-promoted tungsten carbide were catalytically active for the production of EG from cellulose. After that, a series of tungsten-based catalysts, such as Ni-W_xC/MC, Ni-W/SBA-15, Ni-W/SiO₂-Al₂O₃, Ni-WO₃/SBA-15, (WO₃ + Ru/C), (H₂WO₄ + Ru/C) and (ammonium metatungstate (AMT) + Ru/AC), were also found to be effective for catalyzing this reaction^[14–22]. In addition, a significant progress has been made in the design of catalysts and understanding of the catalytic mechanism^[14–25]. Now, it is believed that one-pot conversion of cellulose to EG includes three consecutive reactions: hydrolysis of cellulose to soluble cellooligosaccharides and glucose; retro-aldol condensation of these sugar intermediates to glycolaldehyde; and hydrogenation of glycolaldehyde to EG^[26]. These three

reactions occur at different active sites, and the hydrolysis of cellulose to cellooligosaccharides and glucose is the rate-determining step, which is usually catalyzed by protons in situ generated reversibly from hot water or by additional acid. In contrast, the retro-aldol condensation of soluble sugar intermediates is effectively catalyzed by tungstic compounds. As for the hydrogenation of glycolaldehyde to EG, supported Ni or Ru catalyst is generally used^[26–28]. Thus, the W to Ru or Ni ratio is a crucial factor determining the catalytic performance^[15,17–19,22]. It has been shown that various types of tungstic compounds, such as metal W, W_xC, WO₃, H₂WO₄, AMT and phosphotungstic acid, all exhibit comparable catalytic ability for selective cleavage of C–C bond, suggesting that they contain the same type of active W-based species^[22,26,29]. A detailed investigation shows that part of the tungstic compounds are transformed into soluble tungsten bronze (H_xWO₃) species during the reaction^[29]. Unfortunately, the H_xWO₃ is very unstable in the presence of oxygen. Therefore, it is very difficult to separate it from aqueous solution, and thus, quantify its amount.

Although various types of tungsten species are highly effective for the conversion of cellulose, the obtained EG yields are different. In particular, most of the catalysts contain not only tungstic compounds but also metal Ru or Ni. Is the physical mixture more catalytically effective than the sample prepared by the co-impregnation method? Which type of tungsten species

Received: 28-Dec-2015; Revised: 28-Apr-2016.

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Foundation items: Supported by the Major State Basic Research Development Program of China (973 program, 2012CB215305).

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exhibits the highest efficiency for producing EG? To the best of our knowledge, these questions have not been answered yet.

Glucose is the basic structural unit of cellulose, and hence, an intermediate species during the conversion of cellulose to EG, while cellobiose is the smallest molecule possessing a β -1,4-glycosidic bond. Nonetheless, hydrolysis, C–C bond cleavage and hydrogenation included in the cellulose conversion all occur in the cellobiose conversion. Understanding of the relationship between product distribution and mass transfer limitation is vital to the design of new catalytic system. Therefore, a detailed comparison of glucose and cellobiose conversion processes will be helpful for illustrating the effect of mass transfer limitation on the catalytic properties.

In continuation of our previous work^[17–19], hydrogenolysis of glucose and cellobiose over various kinds of tungsten-based catalysts are systematically investigated here. It will be shown that the Ni-WO₃/SBA-15 prepared by the co-impregnation method is more catalytically effective than the physical mixture of Ni/SBA-15 and WO₃/SBA-15 for the conversion of glucose and cellobiose to EG. In addition, the catalytic performances of WO₃/SBA-15, WO₃ and AMT were investigated, showing that the EG yield was related with the particle size of tungstic compounds.

1 Experimental

1.1 Materials

Glucose (Tianjin Dongliqi Tianda Chem. Reagent Factory, analytic grade), cellobiose (Aladdin Chem. Co. Ltd, analytic grade), tungstophosphoric acid hydrate [H₃O₄₀PW₁₂·xH₂O] (Sinopharm Chem. Reagent Co. Ltd., analytic grade),

ammonium paratungstate [(NH₄)₆W₇O₂₄·6H₂O] (Sinopharm Chem. Reagent Co., Ltd., analytic grade), nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O] (Sinopharm Chem. Reagent Co. Ltd., analytic grade), and SBA-15 (Shanghai Novel Chem. Technol. Co., Ltd.) were used as received without further purification.

1.2 Preparation of catalysts

All the Ni/SBA-15, WO₃/SBA-15 and Ni-WO₃/SBA-15 catalysts were prepared by the conventional incipient wetness impregnation method^[17]. Typically, SBA-15 was impregnated with tungstophosphoric acid hydrate [H₃O₄₀PW₁₂·xH₂O] and nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O] aqueous solution. The impregnated sample was dried at 100°C for 12 h and calcined at 500°C for 3 h. Before the reaction, all the samples were reduced at 500°C for 1 h in a pure H₂ flow. The bulk WO₃ was obtained by calcining the ammonium paratungstate [(NH₄)₆W₇O₂₄·6H₂O] at 500°C for 3 h. The prepared catalysts were designed as x%Ni/SBA-15, y%WO₃/SBA-15 or x%Ni–y%WO₃/SBA-15 with x and y representing the nominal weight loading of metal Ni and WO₃ respectively.

1.3 Catalytic reaction

Conversion of glucose or cellobiose was carried out at 6 MPa H₂ (measured at room temperature) in a stainless-steel autoclave unless specified. Typically, 0.5 g glucose or cellobiose, 0.125 g 10%Ni/SBA-15, 10%Ni-15%WO₃/SBA-15 or designed amount of tungstic compound and 40 g water were first sealed into a 100-mL autoclave.

Table 1 Catalytic results of different catalysts for conversion of glucose

Catalyst	Conversion x /%	Yield w /%				
		EG	1,2-PG	glycerol	sorbitol	mannitol
10%Ni/SBA-15	100	trace	trace	trace	97.2	no
10%Ni/SBA-15+15%WO ₃ /SBA-15 ^a	100	15.2	1.0	2.3	54.5	7.7
10%Ni-15%WO ₃ /SBA-15	100	29.8	2.4	2.9	36.5	7.5

reaction conditions: 0.5 g glucose, 40 g water, 0.125 g catalyst, 175°C, 80 min, 6 MPa H₂ pressure

^a: 0.125 g of 15%WO₃/SBA-15 was used to make sure that it had the same WO₃ content as the 10%Ni-15%WO₃/SBA-15

Table 2 Catalytic results of different catalysts for conversion of cellobiose

Catalyst	Conversion x /%	Yield w /%				
		EG	1,2-PG	glycerol	sorbitol	mannitol
10%Ni/SBA-15	97.8	trace	trace	trace	47.7	no
10%Ni/SBA-15+15%WO ₃ /SBA-15 ^a	100	15.3	1.1	1.8	51.7	4.6
10%Ni-15%WO ₃ /SBA-15	100	40.5	3.4	2.8	18.5	2.0

reaction conditions: 0.5 g cellobiose, 40 g water, 0.125 g catalyst, 190°C, 30 min, 6 MPa H₂ pressure

^a: 0.125 g 15%WO₃/SBA-15 was used to make sure that it had the same WO₃ content as the 10%Ni-15%WO₃/SBA-15

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