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Catalytic Conversion of Glucose Using TiO_2 Catalysts

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Glucose is the most available hexose as it can be obtained from the most abundant and renewable biomass on Earth, cellulose. In addition, glucose can be catalytically transformed into furan derivates such as hydroxymethyl furfural (HMF) and furan dicarboxylic acid (FDCA) which are potential compounds to prepare polymeric materials and biofuels. The catalytic conversion of glucose can proceed via three chemical routes. Firstly, glucose isomerization can produce fructose. Secondly, the dehydration process of glucose to obtain 1,6-anhydroglucose and finally, the dehydration of fructose and small fragments such as glycolaldehyde and dihydroxyacetone through a retro-aldol condensation to obtain HMF [1,2]. It has been shown that basic catalysts are more efficient to convert glucose into fructose. However, acidic properties are also needed to facilitate the dehydration process in order to obtain furan derivates. Titanium oxide catalysts appear to be an appropriate catalyst for an industrial process whereby glucose is converted due to both its acidic and basic properties and its low synthesis cost. Based on this, glucose conversion was studied with a TiO_2 catalyst obtained by a sol-gel method. The reactions were performed as a function of reaction time (2, 4, 6, and 8 h) and temperature (393, 403, 413 and 423 K). N_2 physisorption analysis revealed a mesoporous structure for the titania with a pore diameter range from 10 to 110 Å, superficial area of 128 m^2/g and total pore volume of the $1.7x10^{-7}$ m^3/g. The structural characterization by XRD showed that the titania was present in the anatase polymorph. The catalytic results showed that the lower temperature and reaction time increases the fructose yield. However, significant amounts of HMF were detected at higher temperatures and reaction time.

1. Introduction

The conversion of cellulose into Hydroxymethylfurfural (HMF) and 2,5 dimethylfurane (DMF) comes being widely studied because of the potential use those components to productions of biofuels (Zakrzewska, 2010). The DMF presents higher energy density, higher boiling point, and lower water solubility than ethanol (Roman-Leshkov et al., 2007).

The HMF is obtained of the threefold dehydration of hexoses, like fructose and glucose. Fructose is more reactive than glucose at that reaction (Lewkowski, 2001), but its cost is higher. However, fructose can be obtained from isomerization of glucose. This reaction is studied at food industry to produce corn syrup using enzymatic catalyst. However, the use of enzymatic catalysts has some drawbacks in this process, like narrow operating temperatures, irreversible deactivation, strict feed purification requirements (Roman-Leshkov et al., 2010). On the other side, the non-enzymatic catalysts are characterized for the lower cost, wide conditions of operations, facility of recovery and regeneration.

The first study on isomerization of glucose was in the field of homogeneous catalysis that was performed by Lobry de Bruyn and Alberda Van Ekenstein (1895) using a basic catalyst. This first study and subsequents presented high conversions of glucose, but low selectivity to fructose.

More recently, several studies were presented using heterogeneous catalysts to improve the results obtained with homogeneous catalysts. Moreau et al. (2000) used cation zeolites and hydrotalcites based on the fact that basic catalysts favour the reaction of isomerization of glucose into fructose, they achieved fructose

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selectivities between 80 and 90 %, but glucose conversions were between 15 and 20 %. In the same way, Lecomte et al. (2002) used anion-modified hydrotalcites obtaining fructose selectivities between 15 and 20 %. Another studied was performed by Lima et al (2008) using basic Metallsilicate, they obtained glucose conversions between 27 and 56 % and fructose selectivities between 69 and 85%. In the other way, Moliner et al. (2010) reported the use of tin zeolites and titanium zeolites in water because of the advantage of acid catalysts on the reaction of isomerization of glucose into fructose and Leskov et al. (2010) showed a possible mechanism of glucose isomerization using tin zeolites due to its acid-Lewis properties in water. Their results were glucose conversions of 54 % and fructose selectivities of 57 %.

In addition to the reaction of isomerization of glucose, it is also possible that occur side reactions like dehydration, decomposition and epimerization of glucose or fructose and other reactions from the products obtained of the above reactions. For example, Lecomte et al. (2002) reported the presence of psicose, mannose, and carboxylic acid. Moliner et al. (2010) determined mannose, Watanabe et al. (2005) detected HMF and anhydro glucose and Lourvanij and Rorrer (1997) determined HMF, levulinic and formic acid.

In this way, in the present paper was studied the isomerization of glucose into fructose using TiO_2 catalysts, because this catalyst can have basic characteristics. The reactions were performed in a batch reactor at different time and temperatures. The surface properties of the catalyst were determined using adsorption of N_2 at 77 K and the structure properties were determined using X-ray diffraction (XRD).

2. Experimental Section

2.1 Catalyst preparation

For the synthesis of the catalyst was used Titanium isopropoxide ($C_{12}H_{28}O_4Ti$; 97 %, Aldrich), 2-propanol (Merk) and deionized water. Were mixed 11 mL of titanium isopropoxide and 12 mL of 2-propanol with constant magnetic stirring. After, were added 6 mL of deionized water. The stirring was kept for 1 h. The solution was left to stand for 24 h. Later, it was dried at 353 K for 4 h and calcined at 673 K for 16 h.

2.2 Surface and Textural Properties

The nitrogen adsorption-desorption isotherm of the catalyst was obtained at 77 K from Autosorb 1C, Quantachrome. Initially, the catalyst sample was dried in an oven at 393 K for 12 h. The surface area was determined by BET method (Brunauer et al., 1938), the total pores volume was calculated at relative pressure of 0.95 and the average mesopore distribution was determined by de BJH method (Barrett et al., 1951).

2.3 Structural Properties

The X-ray diffraction (XRD) was carried out using the XPD beamline of the LNLS with a wavelength of 1.54966 Å and energy of 7996.36 eV. The X-ray patterns were acquired using a detector Mythen 1K with 2θ varying from 20 to 900.

2.4 Catalytic tests

The reactions were performed in a metallic reactor heated in a temperature-controlled silicone oil bath on a digital stirring hot plate (IKA), additionally a 25 mL teflon cup was used inside of the metal cup. In all experiments, the reactor was filled with 15 mL of glucose solution at 2 % w/w in water and 0.250 g of catalyst. The reactor was sealed and immersed into silicone oil bath at 393, 403, 413 and 423 K. Zero reaction time was considered at 0.16 h after the reactor submerged. One reaction was performed at each set point temperature and 2, 4, 6, and 8 h. The reactor contents were centrifuged to separate the catalyst and the liquid phase was frozen. Later, they were analyzed by HPLC.

2.5 HPLC

The liquid samples from the reactor were analyzed by high performance liquid chromatography (HPLC). The HPLC system consisted of a Waters 1525 with refraction index (RI) and ultraviolet visible (UV) detectors. With fructose and glucose was used the RI detector with a guard column Micro-Guard Cation PC H refill Cartrigdes, Bio-rad and an analytic column Animex HPX-87H, Bio-rad. Furfural and HMF were analyzed with the UV detector and an analytic column Acclaim 120, C18, Dionex.

2.6 Conversion of glucose and yield of products

The Glucose conversion, X, was determined according to Eq (1) as the ratio between the glucose consumed and the glucose initial.

$$\mathrm{X} = \left(\frac{[\mathrm{G}]\mathrm{o} - [\mathrm{G}]\mathrm{f}}{[\mathrm{G}]\mathrm{o}} \right) \times 100 \tag{1}$$

The yield of products, Ri, was determined according to Eq (2)

$$R = \left(\frac{Mg}{Mi}\right)\left(\frac{\#Ci}{\#Cg}\right)\left(\frac{[i]}{[G]o}\right) \times 100 \qquad (2)$$

Where, Mg is glucose mass molar (180,16 g/mol), Mi is product i mass molar, #Cg is carbon numbers of glucose molecule (6), #Ci is carbon numbers of product i molecule, [i] is product i final concentration, [G]f glucose final concentration and [G]o glucose initial concentration.

3. Results

3.1 Surface and Textural Properties

Figure 1 shows the curve of nitrogen adsorption-desorption isotherm of the TiO_2 catalyst obtained at 77 K and pore size distribution. The curve shows a type IV isotherm that is characteristic of mesopore solids and type hysteresis H_2 that is characteristic of pores with irregular morphology. Surface area was 120 m^2/g, total pore volume $1.7x10^{-7}$ m^3/g and pore diameters are concentrated between 10 to 110 Å.

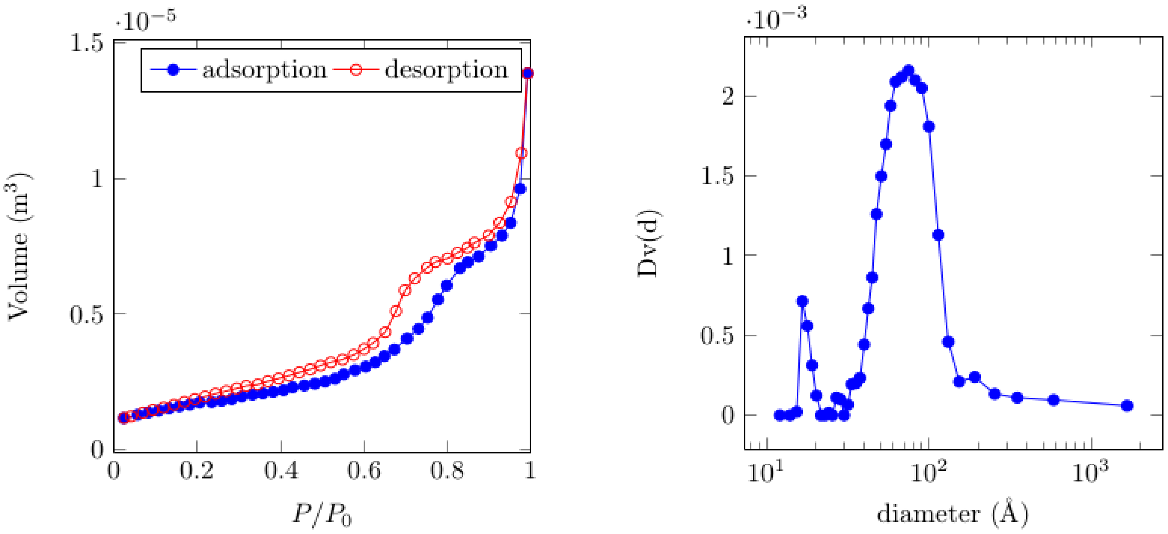

Figure 1. TiO_2 nitrogen adsorption-desorption isotherm at 77 K and pore size distribution

3.2 Structural Properties

Figure 2 shows the catalyst X-ray spectra. The phase of prepared TiO_2 was anatase, and this was determined comparing its spectra with rutile-TiO_2 spectra from Baur (1971) and anatase-TiO_2 spectra from Schwerdtfeger (1972). Watanabe et al. (2005a) reported that anatase-TiO_2 shows higher basic and acid site density than rutile-TiO_2. Basic sites favor the reaction of isomerization of glucose into fructose and acid sites favor the reaction of dehydration of fructose to HMF (Watanabe, 2005a).

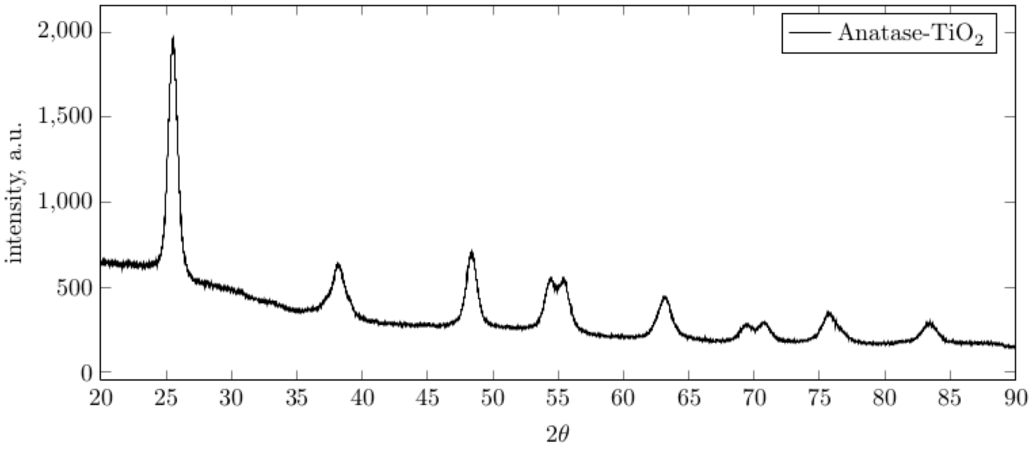

Figure 2. TiO2 XRD pattern

3.3 Catalytic tests

Figure 3 shows the concentrations of glucose versus time at 393, 403, 413 and 423 K. Glucose was continuously converted into other products over the course of the reaction and increased with increasing reaction temperature. The maximum glucose conversion was 85 % at 423 K and 8 h.

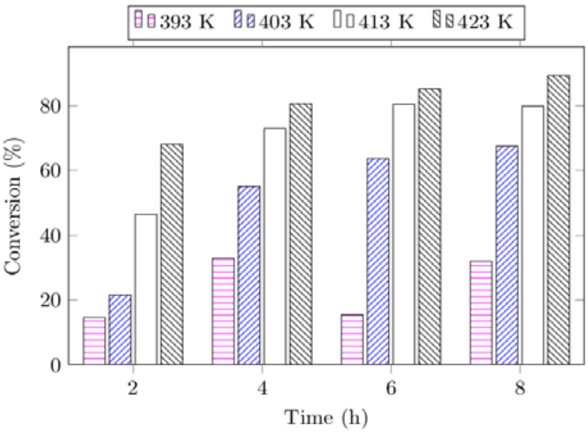

Figure 3. Glucose conversion at 393 (▤), 403 (▨), 413 (□) and 423 K (▧) versus time

Figure 4 shows the products yield versus time at 393, 403, 413 and 423 K. The principal products were fructose and HMF. Other products were levulinic acid, formic acid, glyceraldehyde and furfural, these latter in very low amounts.

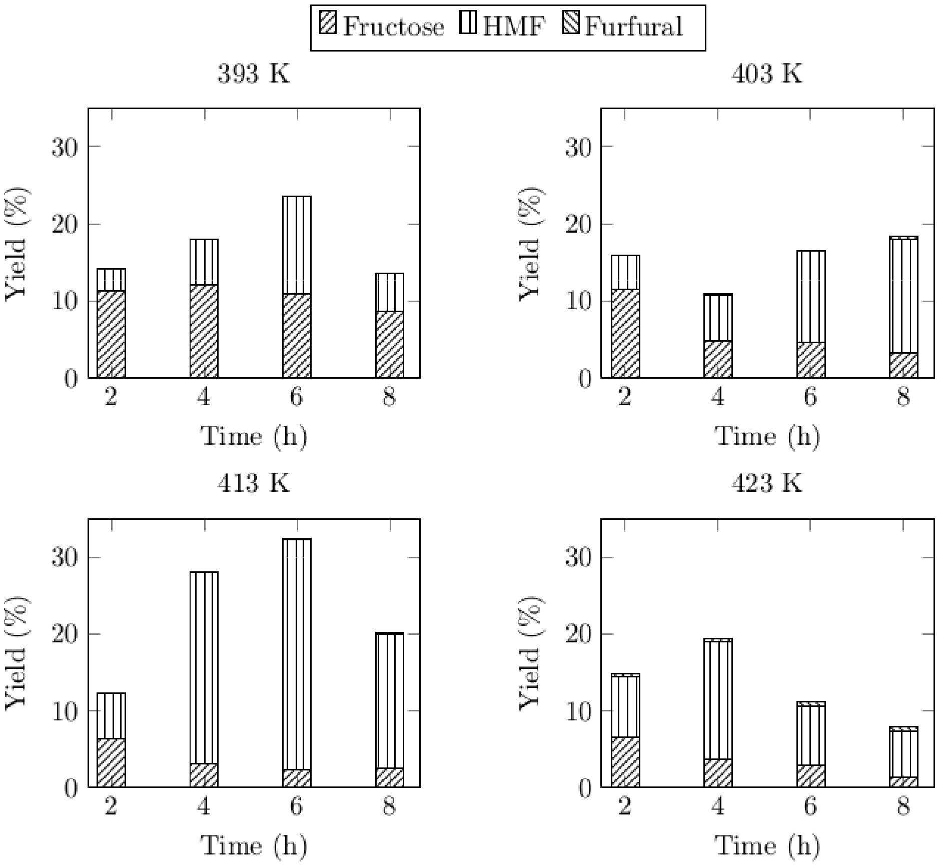

Figure 4. Yield of products from glucose. Fructose (▨), HMF (▥), and furfural (▧)

The fructose yield reached a maximum in all tested temperature, and it was dependent of the temperature of reaction, both at the time of occurrence and the value reached. The value reached was higher at lower temperatures and the time of occurrence was lower at lower temperature. The maximum fructose yield was 12 % at 393 K and 4 h. Similar studies, using TiO_2 and glucose solution in water, performed by Watanabe et al. (2005b) employed higher pressures (2.5MPa) and temperatures (473 K); however, their fructose yield was lower than 5 %. The highest fructose yield obtained in the present work may be due to the lower temperature and pressure employed, because glucose and fructose can be degraded into other products at elevated temperature and pressure.

Moreover, HMF yield also reached a maximum, both its value and time of occurrence depend of reaction temperature. Initially, at higher temperatures its value reached was higher (393, 403 K and 413 K) but at 423 K its value reached was lower. The decrease of HMF yield at 423 K can be possible due to the side reactions from HMF rate are higher than the fructose and glucose dehydration to HMF. On other way, time of occurrence do not shows a trend with increase of temperature. The maximum HMF yield was 30 % at 413 K and 6 h reaction. This value was the largest HMF yield using TiO_2 as catalyst in solution of glucose in water (Hu et al., 2012).

Others products were levulinic and formic acid from dehydration of HMF. Levulinic and formic acid yield continually increased with increasing reaction time and temperature.

4. Conclusion

The effects of temperature and time on the reaction of glucose into fructose using anatase-TiO_2 catalyst were examined. This catalyst has relatively high surface area and it is characterized by having higher basic and acid sites density than rutile-TiO_2. Low temperatures and short periods of reaction increase the yield fructose, but the glucose conversion is lower. The maximum fructose yield was 12 %. High temperatures or reaction time increased the glucose conversion, but also favored side reactions that decrease the fructose yield. However, one of the favored side reactions is the dehydration of fructose into HMF, the maximum HMF yield was 30 %, which envisages the possible use of TiO_2 catalyst, or derived, in the reaction of isomerization of glucose and simultaneously in the dehydration of fructose into HMF.

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