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Selective hydrogenation of D-glucose to D-sorbitol over HY zeolite supported ruthenium nanoparticles catalysts

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ABSTRACT

HY zeolite (HYZ) supported ruthenium (Ru) nanoparticles catalyst (Ru/HYZ) is prepared by simple impregnation method and is characterized by using energy dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), CO chemisorption and inductively coupled plasma (ICP) mass spectrometry. The catalyst Ru/HYZ is evaluated in hydrogenation of D-glucose and hydrogenation experiments to produce a selective product D-sorbitol were conducted batch wise in a three-phase laboratory scale reactor. The kinetics studies of D-glucose hydrogenation using the catalyst Ru/HYZ were carried out. In the operating regime studied the rate of reaction showed first orders dependency with respect to D-glucose and hydrogen. For affording maximum D-glucose conversion, yield and selectivity to D-sorbitol, the reaction conditions were also optimized.

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1. Introduction

D-Sorbitol is one of the most important and popular sugar alcohol which is used as an additive in a variety of foods, drugs, cosmetics products [1–5] and as an intermediate in L-ascorbic acid (vitamin C) synthesis [6]. D-Sorbitol is listed as one of the updated group of platform molecules which included many of original platform molecules such as organic acids (succinic, itaconic, fumaric, etc.), levulinic, and polyols (glycerol, sorbitol, and xylitol) [7] and as well as others (e.g. ethanol, bio-hydrocarbons, furans, etc.) [8,9] that could be transformed into industrially useful chemicals [10–13] such as iso-sorbide [10–12], lactic acid [13] etc. Considering the demand of D-sorbitol, it needs indeed to increase the selective production of D-sorbitol. Conventionally, the D-sorbitol is produced by catalytic hydrogenation of D-glucose using nickel based catalysts e.g. Raney Nickel [14,15]. Raney Ni displayed good catalytic activity and had the properties like low cost, excellent settling, however, it suffered from its leaching and less selective to D-sorbitol rendering the process economically less attractive [2,16–18]. To overcome these drawbacks, many researchers have paid their attentions to develop the catalysts based on other active metals including cobalt, platinum, palladium, rhodium and ruthenium [19–21]. Among the supported metal catalysts studied, only the ruthenium based

catalysts have been found to replace nickel-based catalysts due to their high activity, requirement of lower loading and less deactivation [3,15,17]. Although ruthenium is much more expensive than nickel, it may be of interest for industrial uses as it is more active than nickel, and ruthenium catalyst shows no leaching. Hoffer et al. studied in selective hydrogenation of D-glucose by using carbon supported Ru catalysts. Authors observed that Ru/C catalyst displayed higher activities compared with that of Raney-type Ni [5] and Ru did not leach into the reaction solution. It has also been observed that the catalysts, ruthenium loaded on different supports such as activated carbon [17], Al₂O₃ [22], SiO₂ [23] and MCM-41 [24] and a NiO-modified TiO₂ [25], have different catalytic activities due to their different nature and behavior. An ultrafine Ru-B amorphous alloy catalyst lonely has become more effective in liquid phase hydrogenation of D-glucose [23,26–33], however, their application in industrial catalysis seemed difficult and almost impossible because of their poor thermal stability or/and low surface area.

Zeolites are available in different forms and used as ion exchange, adsorbents and separation agents. Zeolites have also been extensively used as solid catalysts in various organic transformations [34–39] and are considered as suitable host to support the metal nanoparticles exhibiting high activity in hydrogenation of various compounds under mild conditions [40,41]. Because of ordered porous structures and confined void spaces in zeolites, it also restricts the growth of nanoclusters and lead to an increase in the catalyst performance [40–42]. Prompted by the various applications and its properties such as thermal stability, crystalline in

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nature and shape selective etc, HYZ is selected as support material. Here in, we report Ru/HYZ catalyzed selective hydrogenation of D-glucose to D-sorbitol in liquid phase using water as green solvent with added advantages over conventional catalysts. This paper describes the kinetics studies of D-glucose hydrogenation using HYZ supported ruthenium (Ru) catalyst which is prepared by simple impregnation method. The results obtained from the kinetics studies of D-glucose hydrogenation experiments are discussed.

2. Experimental

2.1. Materials

Ruthenium trichloride ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) was purchased from Strem Chemicals, USA. HY zeolite with Si/Al ratio = 80 used as support material (written as HYZ) was purchased by the ZEOLYST International Company, USA. Sodium borohydride (NaBH_4), commercial catalyst Ru(5.0%)/C and ethanol were purchased from M/s Sigma-Aldrich Chemicals, USA. D-Glucose, D-mannose, D-fructose, D-sorbitol were also purchased from M/s Sigma-Aldrich Chemicals, USA. Deionized water is used as a solvent. Hydrogen and nitrogen gases (99.9%) were purchased from Deokyang Co. Ltd and used as such.

2.2. Preparation of catalyst Ru/HYZ

The HYZ supported ruthenium nanoparticles catalyst is prepared by using conventional impregnation–reduction method as reported in the literatures [25]. To incorporate Ru (1.0% by weight) on HYZ support, 1.0 g of HYZ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (26 mg) were placed together with 10 mL ethanol in a two neck 50 mL round bottom flask equipped with a mechanical stirrer and a nitrogen inlet. The resulting mixture was stirred at room temperature under an N_2 atmosphere for a period of 24 h. Then, 0.2 M solution of NaBH_4 in ethanol was added drop wise to reaction mixture with constant stirring; and entire reaction mass was stirred (500 rpm) under N_2 atmosphere for a day at room temperature. Ru(III) was reduced and the Ru (0) nanoclusters were formed which were stabilized by HYZ framework. Finally, catalyst was separated by filtration, washed with ethanol and dried to give dark grey HYZ supported ruthenium catalyst, 1.0 Ru/HYZ (as shown in Scheme 1). The catalysts having different Ru contents such as 0.5 Ru/HYZ, 2.0 Ru/HYZ

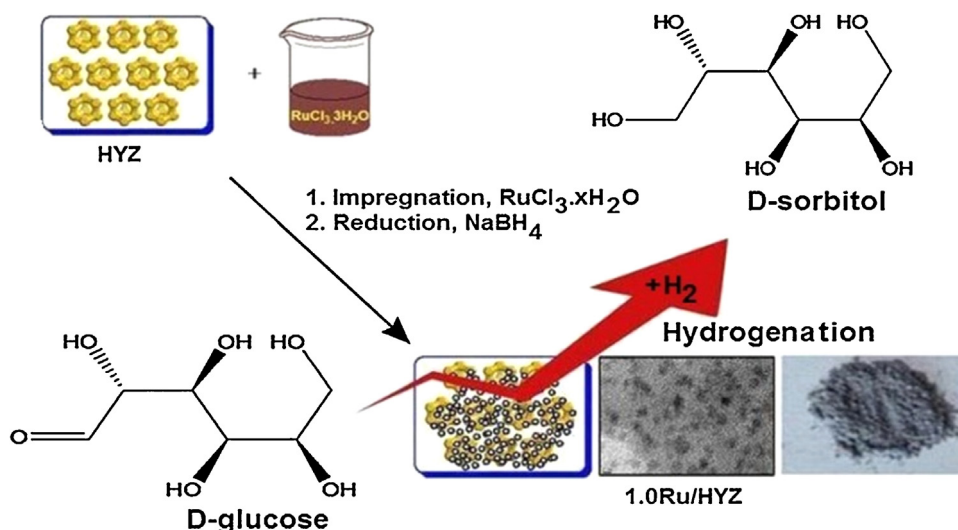
and 3.0 Ru/HYZ were also prepared by as described above methods varying $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ amount. In the entire paper, 0.5 Ru/HYZ, 1.0 Ru/HYZ, 2.0 Ru/HYZ, 3.0 Ru/HYZ correspond to 0.5, 1.0, 2.0 and 3.0 wt% of ruthenium.

2.3. Catalyst characterization

The metal contents (amount of Ru loading) of the catalysts were determined by using EDX, Quantax 200 Energy Dispersive X-ray Spectrometer, Bruker. The amount of metal ions present in the reaction mixture after hydrogenation was analyzed with an inductively coupled plasma-atomic emission spectrometry (Thermo Scientific ICAP 6500 duo). Both, morphology and particle size were determined by the transmission electron microscopy (Maker FEI, Model Technai G2). For the electron microscopy examination, the catalyst samples were dissolved in 2-propanol, dispersed carefully in an ultrasonic bath, and then deposited on carbon-coated copper grids. BET surface area was determined by N_2 adsorption–desorption at -196°C liquid N_2 temperature with a MICROMETRICS, Tristar II analyzer. For each measurement, the sample was degassed at 250°C for 3–4 h, then analyzed at -196°C with N_2 gas at relative pressures (P/P_0) from 0.005 to 1.0 (adsorption) and 1.0–0.1 (desorption). CO chemisorption was carried out by using an instrument model ASAP 2020C V1.09G. Before adsorption of the CO, the catalysts (weighed approximately 0.12 g) were pre-treated in He for 35 min, and in O_2 for 15 min, and were then reduced for 30 min in a (5.0%) H_2/Ar gas flow of 50 mL/min, and in He gas flow for 15 min at 400°C in a reaction chamber. After this pre-treatment, the samples were cooled down to 50°C under He gas flow and CO pulse measurements were carried out using (5.0%) CO/He gas flow of 50 mL/min. Finally, the surface concentration and dispersion of metallic Ru were obtained from the CO pulse analysis data.

2.4. Catalytic hydrogenation of D-glucose

The D-glucose hydrogenation experiments were carried out in 300 mL of batch reactor in the temperature range from 100 to 140°C at hydrogen pressure (20–55 bar) by various stirring rate (400–1200 rpm). The reaction flask was charged with 200 mL of D-glucose solution and catalyst Ru/HYZ. The reaction mixture was deoxygenated by purging the nitrogen gas for 30 min at room temperature. During hydrogenation at different time intervals, the reaction products were analyzed by using a HPLC (Younglin



Scheme 1. Catalyst preparation and hydrogenation of D-glucose to D-sorbitol.

Instrument, Acme 9000) equipped with refractive index (RI) detector and Sugar-Pak column. Deionized water was used as an eluent for the analysis at a flow rate of 0.4 mL/min at 70 °C. D-Glucose (GLS) conversion, selectivity to D-sorbitol (SBTL) and D-mannitol (MNTL) are calculated using following expressions.

$$GLS_{Conv.(\%)} = \left(1 - \frac{\text{mole of GLS at particular time}}{\text{Initial mole of D-glucose}}\right) \times 100$$

$$SBTL_{Selc.(\%)} = \left(\frac{\text{mole of SBTL}}{\text{mole of all products formed}}\right) \times 100$$

$$MNTL_{Selc.(\%)} = \left(\frac{\text{mole of MNTL}}{\text{mole of all products formed}}\right) \times 100$$

3. Results and discussion

The HYZ supported Ru catalysts were characterized by different methods and obtained results are interpreted. The hydrogenation of D-glucose is carried out in liquid phase using Ru/HYZ catalyst. The activity of Ru/HYZ catalyst, effect of stirring rate, metal loading, hydrogen partial pressure, reaction temperature, catalyst amount and reusability of the catalysts were studied systematically in details. The results obtained from these studies are presented and discussed below.

3.1. Interpretation of characterization results

XRD patterns of HYZ support and HYZ supported Ru catalysts are shown in Fig. 1. It can be seen that the XRD patterns of 0.5 Ru/HYZ, 1.0 Ru/HYZ, 2.0 Ru/HYZ, 3.0 Ru/HYZ identical to HYZ support. It indicated that the crystalline nature of the HYZ supported ruthenium catalysts is not significantly affected by the method pursued for the preparation of Ru (0) nanoparticles and insertion.

SEM images of HYZ and 1.0 Ru/HYZ are presented in Fig. 2. It can be seen clearly that the surface morphology of HYZ (Fig. 2a) is similar to its corresponding 1.0 Ru/HYZ catalyst (Fig. 2b). It is stated that ruthenium nanoparticles did not cause any change in surface morphology of HYZ support.

In order to get further information on the morphology of ruthenium nanoparticles, TEM characterization has been performed. The TEM views showed that ruthenium particles were very small with average size around 2.0 nm. These particles are well dispersed throughout the HYZ support (Fig. 3). This is in agreement with the results obtained from CO chemisorptions. The dispersion of metallic ruthenium and metallic surface in case of 1.0 Ru/HYZ with Ru (1.0%) were 23.6% and 86.1 m²/g metal, respectively. These values

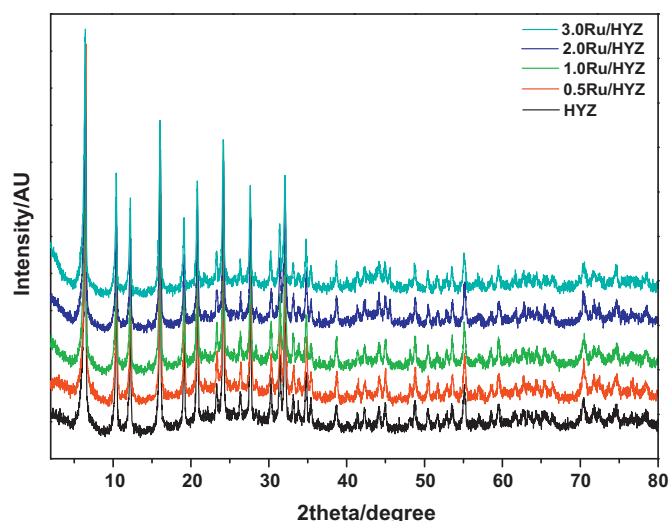


Fig. 1. XRD patterns of HYZ support and HYZ supported Ru catalysts.

of 1.0 Ru/HYZ are higher than those of other reference catalysts, 1.0 Ru/NiO–TiO₂, 1.0 Ru/TiO₂ and 5.0 Ru/C (Table 1). 1.0 Ru/NiO–TiO₂ showed higher values as expected than the values of 1.0 Ru/TiO₂ is due to additive effect of NiO in NiO-modified TiO₂ support. The catalyst 5.0 Ru/C showed higher values of metallic surface area than those of two the reference catalysts, 1.0 Ru/NiO–TiO₂ and 1.0 Ru/TiO₂, is probably due to higher % loading of ruthenium in 5.0 Ru/C. The ruthenium particles size distribution has been also estimated from the measurement of ruthenium particles from the given area of TEM image in Fig. 3 (left side, A) and is presented in (right side, A). It is worth to add that the measurement is only related to the size of ruthenium nanoparticles. In fact, TEM analysis provides the direct information on the metal particles size and is in the range of 2.0–2.5 nm.

As expected, the catalyst (Ru/HYZ) showed only the small decrease in BET surface area from 780 to 778 m²/g determined by N₂ adsorption–desorption and it is due to low loading of ruthenium on HYZ support. The catalyst may have probably low surface area due to the pore blockage by ruthenium metals with high % loading deposit on the support material. Ruthenium content in the catalyst determined by EDX analysis is found as 0.9% less than ruthenium loaded 1.0% experimentally. The ruthenium % loading is also confirmed by EDX-spectrum of 1.0 Ru/HYZ catalyst (Fig. 4).

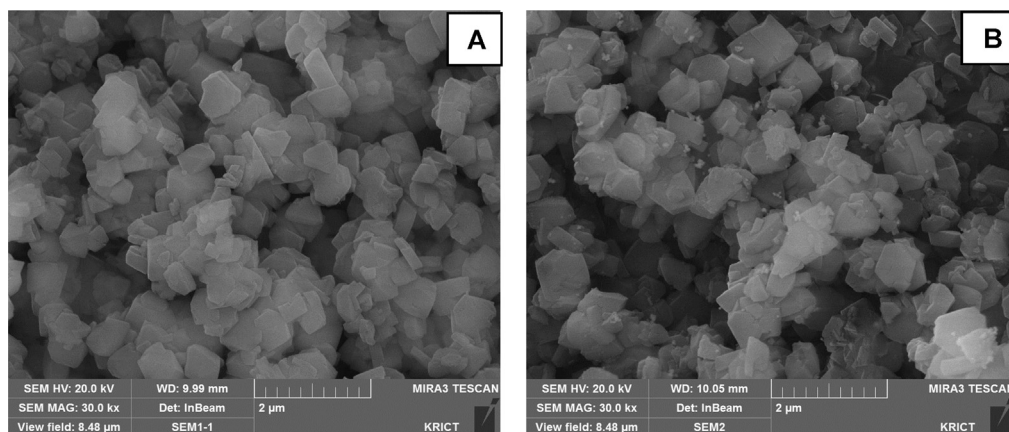


Fig. 2. SEM images of HYZ support (A) and 1.0 Ru/HYZ catalyst (B).

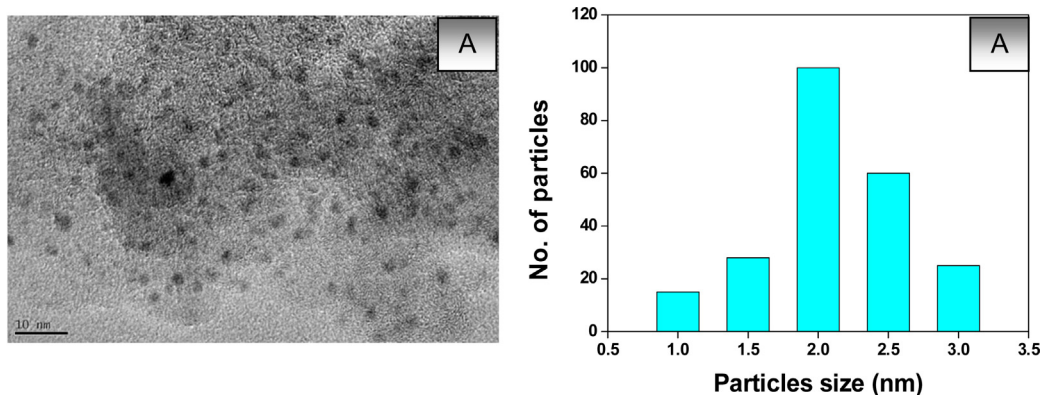


Fig. 3. TEM image (left side, A) of catalyst 1.0 Ru/HYZ and particle size distribution (right side, A).

Table 1
CO chemisorptions data.

Catalysts	Metal dispersion	Metallic surface area (m ² /g sample)	Metallic surface area (m ² /g metal)
1.0 Ru/HYZ	23.6	0.86	86.1
1.0 Ru/NiO–TiO ₂	8.6	0.31	31.3
1.0 Ru/TiO ₂	4.4	0.16	16.1
5.0 Ru/C	6.7	1.22	24.5

3.2. Catalytic activity of the HYZ supported ruthenium (Ru/HYZ) catalysts

Hydrogenation of D-glucose to D-sorbitol looks like simple, but in actual practice, D-glucose is not only converted into a selective product, D-sorbitol, but also converted into many other by-products (as shown in Scheme 2). These by-products become responsible for the deactivation of the catalyst. Some of the by-products are formed by non-catalytic pathways. Lobry de Bruyn–Alberda van Ekenstein rearrangements of D-glucose may give the products of D-mannose and D-fructose. Other by-products such as aldehydes (glycerine aldehyde, glycol aldehyde, formaldehyde, and ketone (dihydroxy acetone) are formed by alkaline cleavages of sugar molecules. D-glucose is converted into 5-hydroxymethylfurfural by

catalytic dehydration process. In liquid phase hydrogenation of D-glucose, the main and by-products are D-sorbitol and D-mannitol, respectively.

The desired product selectivity can be tuned by selecting the active metal and support materials. As ruthenium is used earlier as an active metal in D-glucose hydrogenation [5,17,22–26], however, zeolite as support material is never been used especially in hydrogenation of D-glucose even it is a stable support in hot water up to 150 °C [43]. In our continuous research for the conversion of sugar and sugar alcohols, we thereby selected zeolite-Y as support material for the conversion of xylose to xylitol [44]. It was observed that catalyst activity and selectivity were varied with Si/Al ratio and promising results were achieved with high Si/Al = 80 which has 'mild acidic' nature (weak acid sites) as support with the weak acid sites

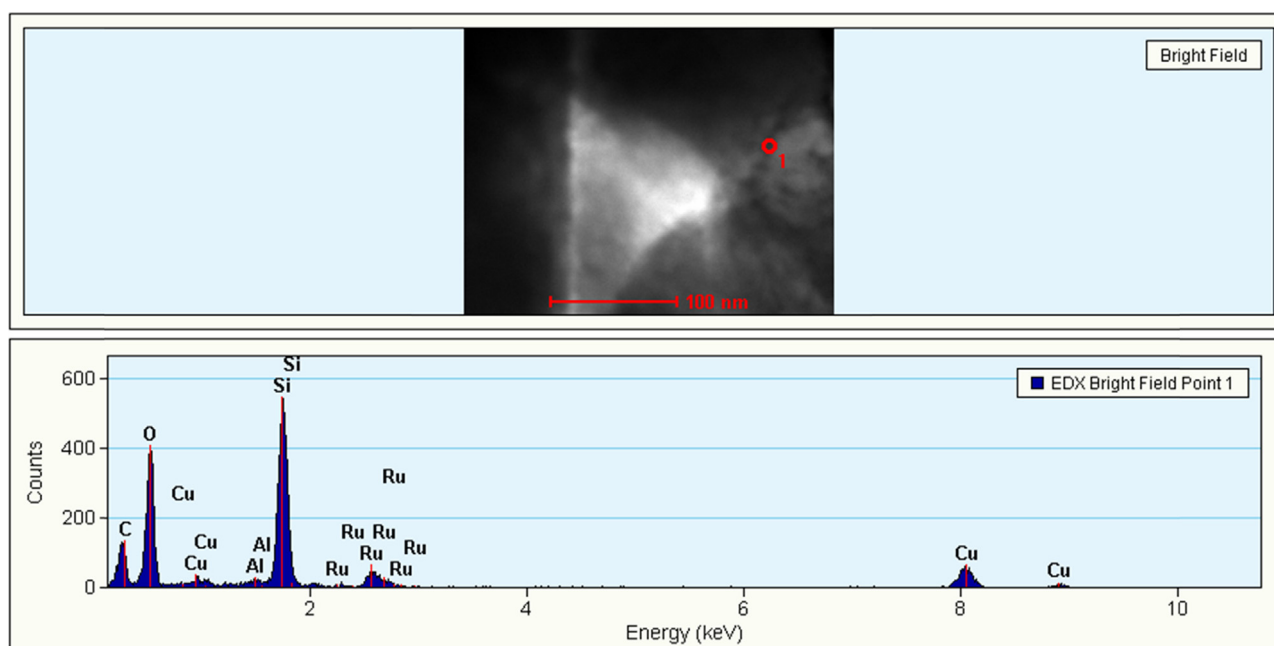
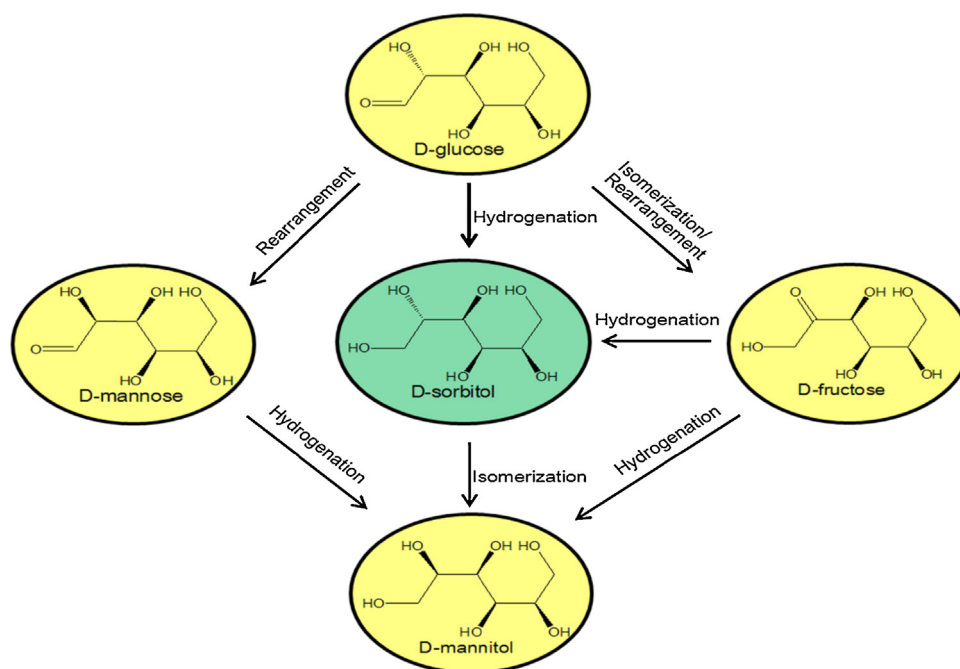


Fig. 4. EDX-spectrum of 1.0 Ru/HYZ catalyst.



Scheme 2. Reaction network of the hydrogenation of D-glucose.

favors the hydrogenation over the isomerization [43]. Considering the promising results of 1.0 Ru/H Zeolite-Y (with Si/Al=80) in the case of xylose hydrogenation, we extended the catalyst application of Ru/HZY in D-glucose hydrogenation. Ru/HZY catalyst is evaluated in hydrogenation of D-glucose and the results are summarized in Table 2. No hydrogenation of D-glucose could occur even after 10 h reaction time (Table 2, entry 1) indicating that ruthenium is active metal centre in hydrogenation of D-glucose. 1.0 Ru/HZY could give maximum value i.e. 1275 turn over frequency (TOF) (Table 2, entry 2), which is higher than the values obtained with the other reference catalysts. Under the conditions described in Table 2, the catalysts 1.0 Ru/NiO-TiO₂, 1.0 Ru/TiO₂ and 5.0 Ru/C could give the values 1183, 1073 and 234 TOF, respectively (Table 2, entry 3–5). The catalyst of ruthenium and zeolite support could alter also the selectivity of D-sorbitol and suppress the formation of other by-products. It is concluded that the acidity (mild acidity) of zeolite support plays an important role in increasing the selectivity to D-sorbitol and leading over competitive reactions.

3.3. Effect of Ru/HZY catalyst loading

The influence of catalyst loading is evaluated by varying the catalyst-to-D-glucose ratio between 1.0 and 3.0 wt% for

hydrogenation experiments (Reaction condition: Temp.= 120 °C, Pressure (H₂)=55 bar, Stir. Speed=1200 rpm and reaction time=120 min), and the results are summarized in Table 3. As expected, D-glucose conversion increased on increasing the catalyst loading from 1.0 to 2.5 wt% and reached up to 100%. The selectivity to D-sorbitol also increased. On further increasing the catalyst ratio from 2.5 to 3.0 wt%, the selectivity to D-sorbitol decreased because of increased formation of D-mannitol. High catalyst loadings favored the isomerization of D-sorbitol, and thus, increased the by-product i.e. D-mannitol. In this experiment, the amount of reactant D-glucose was constant, when excessive amount of catalyst was employed. The highest selectivity to D-sorbitol (98.7%) at complete conversion of D-glucose is found when the catalyst-to-D-glucose ratio (2.5 wt%) was loaded and was sufficient.

3.4. Effect of stirring rate (mass transfer limitation)

The influence of stirring rate to avoid gas-liquid mass transfer limitation was studied by hydrogenating 20 wt% aqueous D-glucose solution at 120 °C temperature and 55 bar hydrogen (H₂) pressure using Ru/HZY catalyst to-D-glucose ratio 2.5 wt% by various

Table 2
Comparison of catalytic data obtained during hydrogenation of D-glucose^a

Entry	Catalysts	Amount (g)	Ru (%)	Conv. (%)		TOF ^d
				GLS ^b	SBTL ^c	
1	HYZ	–	–	–	–	–
2	1.0 Ru/HYZ	1.0	1.0	19.4	97.6	1275
3	1.0 Ru/NiO-TiO ₂	1.0	1.0	18.3	96.0	1183
4	1.0 Ru/TiO ₂	1.0	1.0	17.1	93.2	1073
5	5.0 Ru/C	1.0	5.0	18.8	92.5	234

^a Reaction conditions: Substrate (D-glucose)=40 g, water=160 mL, temp.=120 °C, pressure (H₂)=55 bar, stir. speed=1200 rpm and reaction time=20 min.

^b GLS: D-Glucose.

^c SBTL: D-Sorbitol.

^d TOF: Moles of sorbitol formed per mol of Ru per hour.

Table 3
Variation in amount of catalyst 1.0 Ru/HZY^a.

Amount (g)	Conv. (%)		Sel. (%)	
	GLS ^b	SBTL ^c	MNTL ^d	NI ^e
0.4	86.6	98.2	0.6	1.2
0.6	98.7	98.5	0.6	0.9
0.8	99.9	98.7	0.7	0.6
1.0	100	98.7	0.7	0.6
1.2	100	98.5	1.0	0.5

^a Reaction conditions: Substrate (D-glucose)=40 g, water=160 mL, temp.=120 °C, pressure (H₂)=55 bar, stir. speed=1200 rpm and reaction time=120 min.

^b GLS: D-Glucose.

^c SBTL: D-Sorbitol.

^d MNTL: D-Mannitol.

^e NI: Not identified.

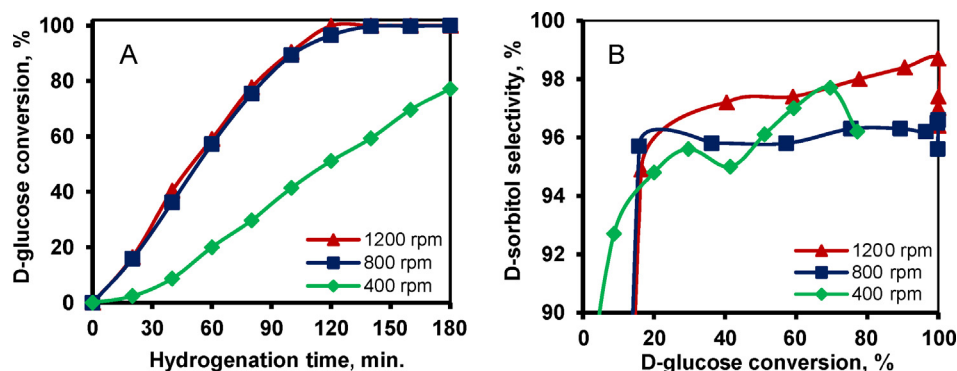


Fig. 5. The influence of impeller rate on D-sorbitol selectivity at 120 °C, 55 bar hydrogen pressure and Ru/zeolite catalyst ratio 2.0 wt% on initial D-glucose.

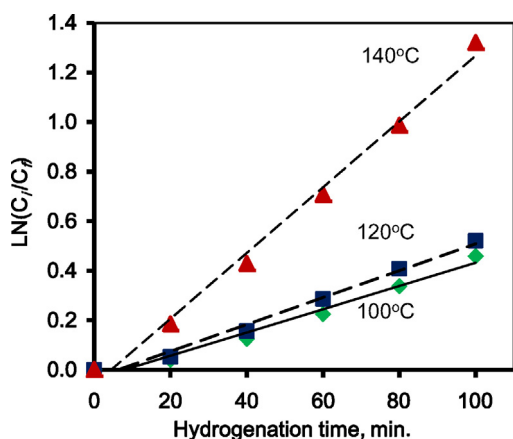


Fig. 6. First order with respect to D-glucose concentration. Reaction conditions: catalyst 1.0 Ru/HYZ = 1.0 g, D-glucose = 20 wt%, temperature (100, 120 and 140 °C), pressure = 40 bar, stirring speed = 400 rpm.

stirring rates (400, 800 and 1200 rpm). The D-glucose conversion (Fig. 5A) and the D-sorbitol selectivity (Fig. 5B) values were hardly affected by changing the impeller rate from 800 to 1200 rpm. The experiment at 400 rpm had clearly a lower reaction rate and gave somewhat lower D-sorbitol selectivity indicating gas–liquid mass transfer limitation. Inefficient mixing in the hydrogenation reactor increased the formation of various other by-products (a reaction network of D-glucose hydrogenation is shown in Scheme 2). Thus, the impeller rate was fixed at 1200 rpm in all of the kinetic experiments to avoid the gas liquid mass transfer limitation. In addition, since TEM views of catalyst Ru/HYZ showed that ruthenium particles were very small with average size around 2.5 nm, it could be considered that there was no the internal diffusion in liquid phase hydrogenation of D-glucose. Furusava et al. also reported that there was no influence of internal diffusion if the Ru-B particles were small (20–50 nm) [45].

3.5. Determination of order reaction

The hydrogenation experiments with 10, 20 and 40 wt% D-glucose solutions were carried out at 120 °C temperature and 40 bar hydrogen pressure using Ru/zeolite catalyst ratio 2.0 wt% on initial D-glucose. The D-glucose concentration did not show any significant influence either on reaction rate and D-sorbitol selectivity at the experimental range, when Ru/zeolite catalyst ratio on initial D-glucose was kept constant i.e. 2.5 wt%. Plot of $\ln(C_i/C_f)$ versus time is linear as shown in Fig. 6. This proves that the hydrogenation of D-glucose follows the first-order with respect to D-glucose concentration. Wisniak and Simon [20] who studied the hydrogenation

of D-glucose over Raney nickel catalyst. They concluded that the reaction showed a first order dependency with respect to D-glucose concentration. Also the obtained result is in agreement with that reported by Crezee et al. [17] who studied the catalytic hydrogenation of D-glucose to D-sorbitol over a 5% Ru/C catalyst in a semi-batch slurry autoclave operating at 100–130 °C and 40–75 bar hydrogen pressure. Authors found that the reaction was a first order with respect to D-glucose concentration.

3.6. Temperature dependency

The effect of the reaction temperature on the D-glucose hydrogenation using catalyst Ru/zeolite was clear. An increased hydrogenation temperature clearly improved the reaction rate at the experiments between 100 and 140 °C. From the Arrhenius plot of $\ln(k_1)$ versus $1/T$, K (Fig. 7) at different temperatures (100, 120 and 140 °C) and constant hydrogen (H_2) pressure 40 bar, it was found that the activation energy (E_a) for D-glucose hydrogenation using catalyst Ru/zeolite was 32.9 kJ/mol which is lower than the values reported in the literatures. Hoffman and Bill studied the hydrogenation of D-glucose in the temperature range from 80 to 130 °C using Raney Ni as a catalyst and reported the activation energy decreased from 82 to 13 kJ/mol with increasing temperature upon a change in the rate-determining step from kinetic control to diffusion limitation [46]. Bizhanov et al. studied the hydrogenation of D-glucose in the temperature range from 80 to 130 °C using catalysts, Raney Ni–Pt and Ni–Rh and reported the activation energies are 50–54 kJ/mol and 38–42 kJ/mol [47]. Tukac studied the catalytic hydrogenation of 40 wt% aqueous solutions of D-glucose in a high-pressure trickle-bed reactor using kieselgur supported nickel catalysts (12% NiO, 2% Cr_2O_3) with a pellet size of

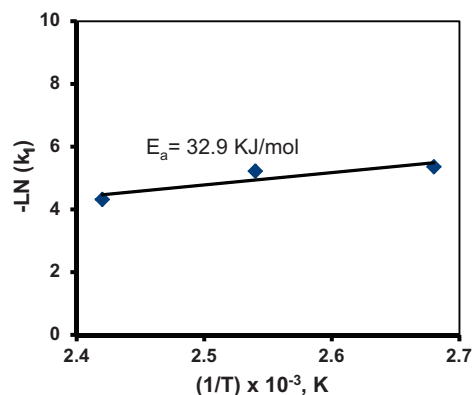


Fig. 7. Arrhenius plots of the initial rates for the D-glucose hydrogenation. Reaction conditions: catalyst 1.0 Ru/HYZ = 1.0 g, D-glucose = 20 wt%, temperature (100, 120 and 140 °C), pressure = 40 bar, stirring speed = 400 rpm.

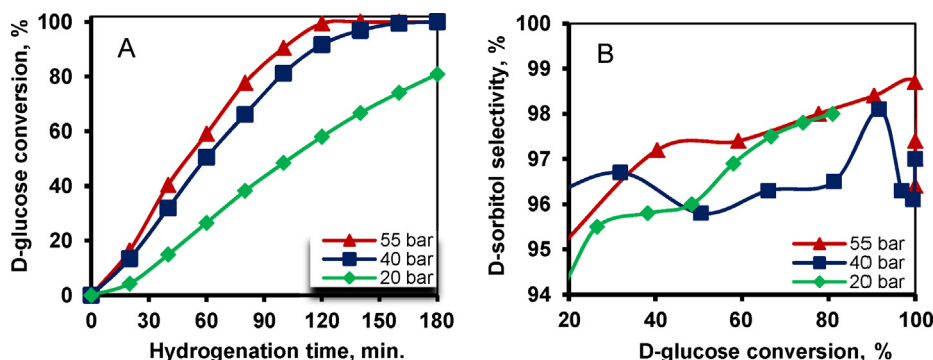


Fig. 8. Influence of hydrogen pressure on D-sorbitol selectivity at 120 °C and Ru/HYZ catalyst ratio 2.0 wt% on initial D-glucose.

2–3 mm. The apparent activation energy amounts to 24–49 kJ/mol, depending on initial D-glucose concentration and density and viscosity of the solution [48]. The author stated that the reaction rate was probably influenced by external mass transfer limitations. Brahme and Doraiswamy studied the hydrogenation of D-glucose in two different temperature ranges from 77–100 °C and 77–146 °C in the pressure range of 0.44–2.1 MPa using Raney–Ni as catalyst (14) and authors reported the activation energies were 44 kJ/mol (77–146 °C) and 6 kJ/mol (77–100 °C). Déchamp et al. studied the catalytic hydrogenation of aqueous solutions of D-glucose in a high-pressure trickle-bed reactor in the range 70–130 °C under 8 MPa and reported an activation energy of about 67 kJ/mol was obtained (17). The low value of activation energy indicated that the Ru/zeolite is very active towards D-glucose hydrogenation to D-sorbitol. At higher temperature, it was observed the D-sorbitol selectivity was decreased significantly. Perhaps, D-sorbitol was converted into D-mannitol and other by-products [49].

3.7. Effect of hydrogen concentration

In hydrogenation of D-glucose to D-sorbitol, it is assumed that hydrogen (H₂) was spread first from air to the liquid. Then, H₂ dissolved in the gas–solution interface and it spread from the liquid to D-glucose in the liquid phase. It is supposed that H₂ did not react with the carbonyl group of D-glucose, but instead was adsorbed by the active centers of the catalyst, producing activated H on the catalyst. Finally, D-glucose reacts with the activated H on the surface of catalyst, which is an irreversible reaction, and then the product desorbs from the catalyst and diffuses into the liquid phase. Therefore, D-glucose hydrogenation proceeds through H₂ dissolution, H₂ diffusion, H₂ adsorption on the active centers of the catalyst, to produce activated H. Finally, the carbonyl group in D-glucose reacted with the activated H on the surface of catalyst to produce D-sorbitol. The hydrogenation experiments with 20 wt% D-glucose solution was also carried out by changing the hydrogen pressure from 20 to 55 bar at 120 °C using Ru/zeolite catalyst ratio 2.0 wt% on D-glucose. An increased hydrogen pressure had positive effect on reaction rate (Fig. 8A) and D-sorbitol selectivity (Fig. 8B).

For determination of the order of reaction with respect to hydrogen pressure, the conversion rate (*r*) was expressed as

$$r_g = -k_1 (c_g)^\beta (P_{H_2})^\alpha \quad (1)$$

where, *k*₁ is rate constant, *c*_g and *P*_{H₂} are glucose concentration (mol/L) and hydrogen concentration, respectively.

As observed the process is first order with respect to D-glucose concentration i.e. β=1. The mass balance of D-glucose can be expressed by

$$dc_g/dt = \rho \times r_g = -k_1 \rho \times (c_g)^\beta (P_{H_2})^\alpha \quad (2)$$

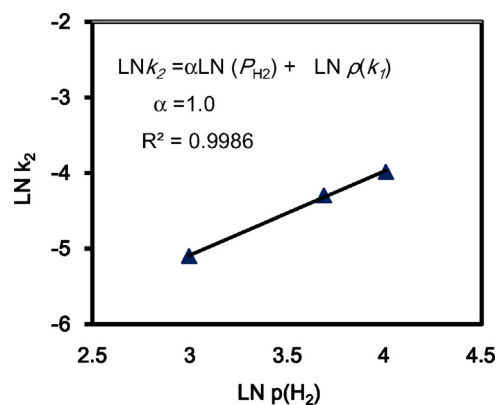


Fig. 9. Determination of reaction order with respect to hydrogen pressure.

where, ρ is density of catalyst.

Further, at constant pressure, (4) and (5) can be derived

$$k_2 = k_1 \times \rho \times (P_{H_2})^\alpha \quad (3)$$

$$LN(C_i/C_f) = k_2 t \quad (4)$$

To reveal the rate dependence on hydrogen pressure, Eq. (4) was rewritten to a logarithmic form (Eq. (5)).

$$LN k_2 = \alpha LN(P_{H_2}) + LN(\rho k_1) \quad (5)$$

The D-glucose hydrogenation at 120 °C was proved to be of first order with respect to hydrogen (Fig. 9). This result is very good agreement with the results reported by Hofmann and Bill et al. [27,44]. Authors studied the hydrogenation of D-glucose in a slurry batch reactor in the temperature range of (80–130 °C) using

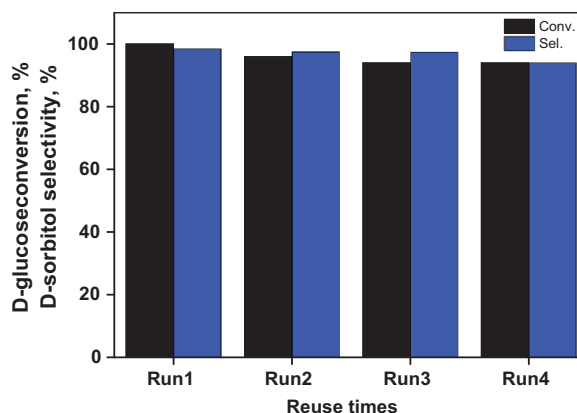


Fig. 10. Reusability test of 1.0Ru/HYZ catalyst.

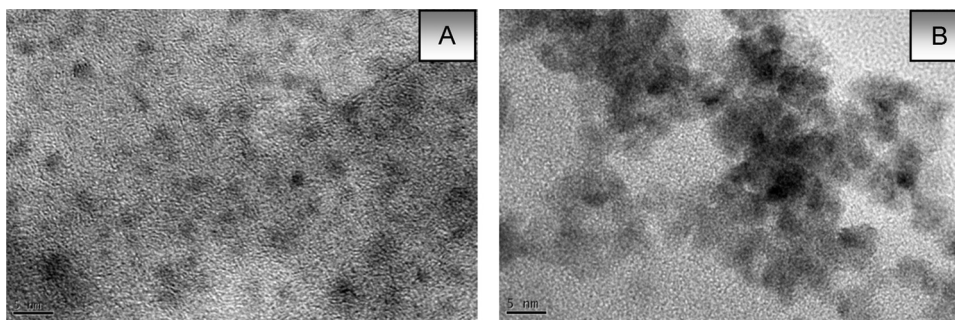


Fig. 11. TEM images of the fresh catalyst (A) and the catalyst after four cycles (B).

Raney-nickel as a catalyst. The authors found a first order dependency in both D-glucose and hydrogen. Crezee et al. studied the catalytic hydrogenation of D-glucose over the 5 wt% Ru/C. They also reported a first order dependency with respect to hydrogen, even though there was a shift in order of reaction with respect to D-glucose concentration.

3.8. Re-usability test of Ru/HYZ catalyst

The reusability of the Ru/HYZ catalyst for the hydrogenation of D-glucose was also investigated under the optimized reaction conditions, and the results are presented in Fig. 10. The catalyst could be reused at least four times, the catalyst-D-glucose ratio was always the same after each run, without notable changes in activity and selectivity to D-sorbitol. It has also reported that both D-sorbitol and D-mannitol had a little effect on the activity of the catalyst [50]. On comparing the TEM images of the fresh catalyst (as shown in Fig. 11a) and the catalyst after four cycles (as shown in Fig. 11b), it could be seen that the change of the morphology of the catalyst was not considerable. The excellent stability of the catalyst may result from the strong interaction between the HYZ support and active species.

4. Conclusions

Hydrogenation of D-glucose to D-sorbitol was carried out using an active catalyst Ru/HYZ and low value of activation energy i.e. 32.9 kJ/mol for hydrogenation of D-glucose to D-sorbitol is obtained. The kinetics experiments gave the first reaction orders with respect to D-glucose and hydrogen. The selectivity values improved slightly as the hydrogen pressure increased and the reaction temperature decreased at the experimental range. High D-sorbitol selectivity (up to 98.7%) can be achieved. A small amount of D-mannitol was formed as by-product. Overall, it is concluded that catalyst Ru/HYZ can be used for all industrial applications in hydrogenation of carbohydrate sugar to sugar alcohols.

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