Contents lists available at SciVerse ScienceDirect

# Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

# Selective hydrogenation of D-mannose to D-mannitol using NiO-modified $TiO_2$ (NiO-TiO<sub>2</sub>) supported ruthenium catalyst

## Dinesh Kumar Mishra, Jin-Soo Hwang\*

Bio-refinerery Research Center, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

#### ARTICLE INFO

Article history: Received 13 August 2012 Received in revised form 25 October 2012 Accepted 28 November 2012 Available online 14 December 2012

Keywords: D-mannose D-mannitol Kinetics Hydrogenation Ruthenium NiO-modified TiO<sub>2</sub>

## ABSTRACT

NiO-modified TiO<sub>2</sub> (NiO-TiO<sub>2</sub>) supported ruthenium catalyst Ru/(NiO-TiO<sub>2</sub>) is prepared by simple impregnation method and characterized by using energy dispersive X-ray analysis (EDX/EDS), temperatureprogrammed reduction (TPR), inductively coupled plasma (ICP) mass spectrometry, transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and CO chemisorption. The catalyst Ru/(NiO-TiO<sub>2</sub>) is evaluated in D-mannose hydrogenation and hydrogenation experiments to produce a selective product D-mannitol were carried out batch wise in a three-phase laboratory scale reactor. A tentative mechanism for reduction of D-mannose is presented. The kinetics of D-mannose hydrogenation to D-mannitol using catalyst Ru/(NiO-TiO<sub>2</sub>) was studied. The kinetic data were modeled by zero, first and second-order reaction equations. A set of four experiments was also carried out to test the deactivation of the catalyst. For affording maximum D-mannose conversion, yield and selectivity to D-mannitol, the reaction conditions are optimized.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Several attempts were made by researchers earlier to develop the catalysts based on nickel as an active metal (the catalysts, Raney Ni or supported/promoted nickel catalysts) [1–5] in hydrogenation of sugars to their corresponding sugar alcohols [6,7]. But, the nickel based catalysts were found to have some disadvantage (leaching) resulting in loss of activity and high metal content in the product solution [8,9]. Therefore, in recent years the catalysts based on ruthenium due their higher activities were evaluated in the hydrogenation of sugars to sugar alcohols (i.e. D-sorbitol, xylitol, lactitol, etc.) [10–17]. Off these, a sugar alcohol D-manntiol, similar to D-sorbitol, is of the industrial important since D-mannitol is also extensively used in food and pharmaceutical industries [18-22]. It has excellent properties such as non-toxic, non-hygroscopic and low caloric sugar. D-mannitol is present in small quantities in most fruits and vegetables [23-27]. Besides small amount of D-mannitol can be obtained naturally from their sources, commercial large scale production of D-mannitol was relied on catalytic hydrogenation of an appropriate starting material either D-fructose/invert sugar (D-fructose/D-glucose mixture) or D-mannose. Most of the studies were focused for the production of D-mannitol by catalytic hydrogenation of aqueous solutions either of D-fructose [28] or invert sugar (D-fructose/D-glucose mixture) [29,30] at high

pressure and a high temperature. However, very little attention is paid for direct hydrogenation of D-mannose to D-mannitol and hydrogenation experiments to produce D-mannitol is scantly available in the literature [31]. Since D-mannose is a natural aldohexose and a building block of vegetable polysaccharides, therefore D-mannose possesses industrial relevance for the production of D-mannitol. It is mainly used as a sugar substitute and for pharmaceutical purposes. D-mannose is chosen here as a starting material for the production of D-mannitol (as represented in Scheme 1).

Our aim of the work was to evaluate (NiO-TiO<sub>2</sub>) supported ruthenium catalyst Ru/(NiO-TiO<sub>2</sub>) in direct hydrogenation of D-mannose to D-mannitol. In kinetic study of D-mannose hydrogenation, both order of reaction and activation energy were also determined. A set of four experiments was carried out to test the deactivation of the catalyst.

#### 2. Experimental

#### 2.1. Materials

Ruthenium chloride (RuCl<sub>3</sub>·*x*H<sub>2</sub>O) was purchased from Strem Chemicals, Newburyport, MA01950 (USA). The nickel chloride, D-mannose and D-mannitol were purchased from Sigma–Aldrich company, Inc, (USA). The support titanium (IV) oxide (rutile type) (TiO<sub>2</sub>), purity – 99.9%, shape fine powder ca. 1–2 micron purchased from Degussa is used after drying at 110 °C. De- ionized water was used as solvent for making all solutions.





<sup>\*</sup> Corresponding author. Tel.: +82 42 860 7382; fax: +82 42 860 7676. *E-mail address*: jshwang@krict.re.kr (J.-S. Hwang).

<sup>0926-860</sup>X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2012.11.042



Scheme 1. A schematic approach for the preparation of active catalyst (Ru/NiO-TiO<sub>2</sub>) used in hydrogenation of D-mannose to produce D-mannitol.

#### 2.2. Catalyst Ru/(NiO-TiO<sub>2</sub>) preparation

The preparation of novel catalyst Ru/(NiO-TiO<sub>2</sub>) was carried out by impregnation method using ruthenium chloride and new class of NiO-modified TiO<sub>2</sub> support [11,16]. The proposed support material (NiO-TiO<sub>2</sub>) was prepared by the following procedure: required amount (4.8 g) of TiO<sub>2</sub> was immersed into aqueous solution nickel chloride (0.55g) under magnetic stirring. Then, the resulting mixture was dried at 110°C overnight and after complete drying the sample was oxidized in air at 500 °C for 10 h to obtain NiO-modified TiO<sub>2</sub> support (NiO-TiO<sub>2</sub>) (Scheme 1). The calculated amount of (NiO-TiO<sub>2</sub>) was further re-impregnated with aqueous solution of ruthenium (III) chloride (0.52 g) and was kept in an oven at 110 °C overnight. The catalyst Ru/(NiO-TiO<sub>2</sub>) thus prepared was reduced in a continuous flow of (5.0%) H<sub>2</sub>/Ar at 200 °C (temperature determined from temperature-programmed reduction experiment) for 3 h and then used immediately for the hydrogenation of D-mannose.

#### 2.3. Hydrogenation of D-mannose

10 wt% D-mannose solution was prepared by dissolving 20 g of D-mannose in 180 ml de-ionized water. This solution was mixed with 1.0 g of catalyst Ru/(NiO-TiO<sub>2</sub>) to form the reaction slurry and thereafter the hydrogenation experiments of D-mannose were conducted in a 300 mL. The hydrogen gas was purged into the reactor at 2.0 MPa H<sub>2</sub> pressure to deoxygenate the reaction mixture followed by stirring (400 rpm for 30 min) at room temperature and then pressure was released. The hydrogenation was initiated by stirring the reaction mixture at constant impeller speed of 1200 rpm and was continued for 240 min at temperature of 120 °C and hydrogen  $(H_2)$  pressure of 40–55 bar. At the end of hydrogenation, the solution was cooled and the catalyst was allowed to settle at the bottom of reaction flask. The above mentioned procedure was followed with other catalyst Ru/TiO<sub>2</sub> which was reduced at 320 °C [11,16]. The supernatant solution was filtered and then analyzed using a HPLC (Younglin 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. The temperature of RI detector was maintained at 35 °C throughout the analysis.

Before starting the TPR experiments, the samples were dried at 120 °C for 1 h under Ar flow and then cooled to room temperature. The (10%)  $H_2$ /Ar was used as reducing gas at a continuous flow rate of 10 mL/min.

#### 2.4. Catalysts 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 stability of catalysts (before and after reactions) was determined with X-ray diffraction (RIGAKU, Miniflex Instruments). 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<sub>2</sub> adsorption-desorption at 77 K liquid N<sub>2</sub> temperature with a MICROMETRICS, Tristar II analyzer. For each measurement, the sample was degassed at 250 °C for 3–4 h, then analyzed at 77 K with N<sub>2</sub> gas at relative pressures  $(P/P_0)$  from 0.005 to 1.0 (adsorption) and 1.0 to 0.1 (desorption). CO chemisorption was carried out by using an instrument model ASAP 2020C V1.09 G. Before adsorption of the CO, the catalysts (weighed approximately 0.12 g) were pre-treated in He for 35 min, and in O<sub>2</sub> for 15 min, and were then reduced for 30 minin 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.



**Fig. 1.** XRD patterns of TiO<sub>2</sub>, (NiO-TiO<sub>2</sub>), Ru/NiO-TiO<sub>2</sub> (fresh sample), and Ru/NiO-TiO<sub>2</sub> (R) (after hydrogenation).



**Fig. 2.** TEM image of the catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub>).

#### 3. Results and discussion

#### 3.1. Catalyst characterization

The X-ray diffraction patterns of  $TiO_2$ ,  $(NiO-TiO_2)$ , catalyst  $Ru/(NiO-TiO_2)$  and catalyst  $Ru/NiO-TiO_2$  (R) (R: after



Fig. 4. H<sub>2</sub>-TPR profile of catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub>.

hydrogenation) are shown in Fig. 1. It is seen from this figure that the XRD profiles of TiO<sub>2</sub> support and NiO-modified TiO<sub>2</sub> support have obvious differences. The presence of characteristics NiO peaks appeared at  $2\theta$  values of  $37^{\circ}$ ,  $43^{\circ}$ ,  $62^{\circ}$ ,  $75^{\circ}$  and  $79^{\circ}$  indicates successful modification of TiO<sub>2</sub> support with nickel chloride salt precursor. In addition, the XRD profiles of NiO-TiO<sub>2</sub> and its catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub> look alike. The metallic Ru in the catalysts (before and after hydrogenation) could not be detected as Ru loadings less than 5.0% are always covered by NiO-modified TiO<sub>2</sub> support making it difficult to determine [32].

TEM view of [Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub>] catalyst showed that the size of ruthenium particles was very small 2.0 nm or less [11,16]. These ruthenium particles were distributed over NiO particles (10–12 nm) of (NiO-TiO<sub>2</sub>) support (Fig. 2). The above statement is in agreement with the results obtained from CO chemisorption [11,16]. It has been found that the dispersion of ruthenium over NiO-TiO<sub>2</sub> support is 63.2%. In order to confirm the existence all three metals Ru, Ni and Ti, EDX analysis was also carried out and the spectrum is presented in Fig. 3. The spectrum undoubtedly shows the presence of all three components Ru, Ni and Ti of the catalyst [Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub>].

The reducibility of the catalyst prepared was examined by TPR. Fig. 4 showed that the profile of [Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub>] displayed a peak at 150 °C which is attributed to the reduction of Ru<sup>3+</sup>  $\rightarrow$  Ru<sup>0</sup> and the second peak at 378 °C is due to the reduction of



Fig. 3. EDX spectrum of the catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub>.

## Table 1

Time versus D-mannose concentration data using initial D-mannose concentration C	$L_i = 1$	0 wt% (0.555 mol/L),	catalyst ratio =	5.0 wt% g at pressure =	40 bar.
--	-----------	----------------------	------------------	-------------------------	---------

	Temp. (°C)									
	100 ° C	100 °C			120 °C			140°C		
Time (min)	$C_f$ (mol/L)	$LN(C_i/C_f)$	$1/C_f$	$C_f$ (mol/L)	$LN(C_i/C_f)$	$1/C_f$	$C_f$ (mol/L)	$LN(C_i/C_f)$	$1/C_f$	
0	0.555	0.000	1.802	0.555	0.000	1.802	0.555	0.000	1.802	
30	0.536	0.035	1.865	0.491	0.122	2.035	0.475	0.155	2.104	
60	0.490	0.125	2.042	0.407	0.310	2.456	0.347	0.471	2.886	
90	0.447	0.216	2.236	0.338	0.495	2.955	0.259	0.763	3.865	
120	0.403	0.320	2.480	0.272	0.712	3.670	0.192	1.062	5.208	

oxidized ruthenium deposited on the surface of NiO-TiO<sub>2</sub> support. There is an additional peak observed at 425 °C which is attributed to delayed reduction of Ni<sup>2+</sup>  $\rightarrow$  Ni<sup>0</sup> [33]. It is clear from the TPR data that a temperature of ~200 °C is enough for the reduction of Ru<sup>3+</sup>  $\rightarrow$  Ru<sup>0</sup> without affecting the NiO- modified TiO<sub>2</sub> support.

#### 3.2. Determination of order of reaction and activation energy

For determination of the order of reaction, equations of zero, first and second-order reaction are used [34]. These equations can be written as follows:

Zero-order reaction equation

$$C_f = C_i - k_0 t \tag{1}$$

where  $C_i$  = Initial concentration of D-mannose in reaction solution (mol/L),  $C_f$  = final concentration of D-mannose in reaction solution (mol/L),  $k_0$  = zero order rate constant (mol L<sup>-1</sup> min<sup>-1</sup>), t = temperature.

First- order reaction equation

$$LN\left(\frac{C_i}{C_f}\right) = k_1 t \tag{2}$$

where  $k_1$  = first-order rate constant (min<sup>-1</sup>).

Second-order reaction equation

$$\frac{1}{(C_f)} = \left(\frac{1}{(C_i)} + k_2 t\right) \tag{3}$$

where  $k_2$  = second-order rate constant (1 mol<sup>-1</sup> min<sup>-1</sup>).

Table 1 shows time versus D-mannose concentration data using initial D-mannose concentration  $C_i = 10$  wt% (0.555 mol/L) and catalyst amount of 1.0 g, at hydrogen (H<sub>2</sub>) pressure of 40 bar and different temperatures of 100, 120 and 140 °C. This table shows that the D-mannose concentration decreased with increasing the temperature of reaction, due to the increase of D-mannose conversion. An increase in temperature from 100 to 140 °C at constant time of 120 min, leads to a decrease in D-mannose concentration from 0.403 to 0.192 mol/L. Plot of final D-mannose concentration ( $C_f$ ) and (1/( $C_f$ )) versus time for zero and second- order, respectively, are nonlinear as shown in Figs. 5 and 7, while plot of LN( $C_i/C_f$ ) versus time for Eq. (2) is linear as shown in Fig. 6. This proves that the reaction D-mannose hydrogenation follows the first-order in nature.

The activation energy is calculated by using Arrhenius equation which can be written as follows:

$$k_1 = Ae^{(-E/RT)} \tag{4}$$

where A = exponential factor, E = activation energy (KJ mol<sup>-1</sup>), and R = gas constant (8.3145 mol<sup>-1</sup> K<sup>-1</sup>)

The first-order reaction rate constants (kinetic constants) (Table 2) are obtained from the slope of curve, plot of  $LN(C_i/C_f)$  against time (min) at different temperatures. From Arrhenius plot of  $LN(k_1)$  versus 1/T, K as shown in Fig. 8, activation energy is calculated as  $48.2 \text{ kJ} \text{ mol}^{-1}$ . The low value of activation energy may



**Fig. 5.** Test for zero order of reaction; catalyst = 1.0 g, D-mannose = 10 wt%, impeller speed = 1200 rpm and hydrogen (H<sub>2</sub>) pressure = 40 bar.

suggest the effectiveness and high activity of NiO-modified TiO<sub>2</sub> supported ruthenium novel catalyst in D-mannose hydrogenation.

The catalytic activities calculated in terms of initial rate  $(2958.3 \text{ m} \text{mol} \text{h}^{-1} \text{g}_{\text{Ru}}^{-1})$  and TOF  $(298.9 \text{ h}^{-1})$  for NiO-modified TiO<sub>2</sub> supported ruthenium novel catalyst Ru/NiO-TiO<sub>2</sub> are also higher than those for the catalyst Ru/TiO<sub>2</sub> (Table 3). The additive effect of NiO (NiO loading of 5.0 wt%) in NiO modified TiO<sub>2</sub> support plays an important role to raise the reaction rate and selectivity to the main product i.e. p-mannitol. In the NiO-modified TiO<sub>2</sub> support, leading to the formation of large numbers of unsaturated NiO sites.



**Fig. 6.** Test for first order of reaction; catalyst = 1.0 g, D-mannose = 10 wt%, impeller speed = 1200 rpm and hydrogen (H<sub>2</sub>) pressure = 40 bar.



**Fig. 7.** Test for second order of reaction; catalyst = 1.0 g, D-mannose = 10 wt%, impeller speed = 1200 rpm and hydrogen (H<sub>2</sub>) pressure = 40 bar.

Table 2
Effect of temperature on D-mannose hydrogenation at D-mannose concentration
$C_i = 10 \text{ wt\%} (0.555 \text{ mol/L})$ , catalyst ratio = 5.0 wt% g at pressure = 40 bar.

Temp. (°C)	$k_1 ({ m min}^{-1})$	$(1/T) \times 10^{-3}$ (K)	$LN(k_1)$
100°C	0.003	2.68	-5.80914
120°C	0.007	2.54	-4.99083
140°C	0.014	2.42	-4.30507



**Fig. 8.** Effect of temperature on reaction rate; catalyst = 1.0 g, p-mannose = 10 wt%, impeller speed = 1200 rpm and hydrogen (H<sub>2</sub>) pressure = 40 bar.

The thus-formed unsaturated NiO sites act as efficient adsorption sites on the surface of catalyst where D-mannose reacts with the activated H.

# 3.3. Tentative mechanism for reduction of D-mannose to D-mannitol

The hydrogenation of p-mannose to p-mannitol using the NiO-TiO<sub>2</sub> supported ruthenium catalyst is a gas-liquid-solid threephase catalytic reaction. The mechanism of reducing D-mannose with H<sub>2</sub> on the catalyst surface is shown in Scheme 2. Hydrogen  $(H_2)$  was spread first from air to the liquid membrane. Then,  $H_2$ dissolved in the gas-solution interface and it spread from the liquid membrane to D-mannose in the liquid phase. It is supposed that H<sub>2</sub> did not react with the carbonyl group of D-mannose, but instead was adsorbed by the active centers of the catalyst, producing activated H on the catalyst [32]. Finally, D-mannose 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-mannose hydrogenation proceeds through H<sub>2</sub> dissolution, H<sub>2</sub> diffusion, H<sub>2</sub> adsorption on the active centers of the catalyst, to produce activated H. Finally, the carbonyl group in D-mannose reacted with the activated H on the surface of catalyst to produce D-mannitol.

# 3.4. Optimization of reaction conditions (D-mannose hydrogenation)

D-mannose hydrogenation experiments were carried out at constant stirring speed of 1200 rpm. Since TEM views of ruthenium catalyst showed that ruthenium particles were very small with average size around 2.0 nm, the mass transfer effects could be neglected. Furusava et al. reported that there was no influence of internal diffusion even in liquid phase hydrogenation of D-glucose if the Ru-B particles were small (20–50 nm) [13,35].

The effect of reaction times on the hydrogenation of D-mannose is shown in Fig. 9. The D-mannose conversion increased when the reaction time was increased up to the 260 min; D-mannose was completely converted. At the early period of the hydrogenation, Dmannose was converted into D-mannitol and yield/selectivity to D-mannitol reached the highest level at 240 min. After 260 min, the mannitol yield declined as the reaction progressed. Perhaps the product D-mannitol degrades into other products during this process. Hence, the optimum reaction time was 240 min.

The relationship between catalyst amount (catalyst ratio, wt% on initial D-mannose concentration) and D-mannose conversion or yield/selectivity D-mannitol, is indicated in Fig. 10. Figure shows that the D-mannitol yield increased with an increase in the amount of catalyst up to the 5.0 wt%, when further increasing catalyst amount from 5.0 to 6.25 wt%, the yield did not change significantly, and D-mannose had already been converted into D-mannitol completely. In this experiment, the amount of reactant D-mannose was constant, when excessive dosage of catalyst was employed, no high conversion rate could be found. Hence the D-mannitol yield was relatively stable when the dosage of catalyst was 5.0 wt%. The

Catalysts	Catalysts (g)	Conversion (%)	Initial rate/ $g_{Ru} \ (m \ mol \ h^{-1} \ {g_{Ru}}^{-1})^a$	$TOF^{b}(h^{-1})$
No Catalyst	-	-	_	-
NiO(5.0%)-TiO <sub>2</sub>	1.0	-	-	-
Ru(1.0%)/NiO(5.0%)-TiO2	1.0	26.7	2958.3	298.9
Ru(1.0%)/TiO <sub>2</sub>	1.0	18.4	2044.2	206.6

<sup>a</sup> Mannose 10 (wt%), time = 60 min, pressure = 40 bar and temp. =  $120 \circ C$ .

Catalytic activity data obtained during hydrogenation of D-mannose.

<sup>b</sup> TOF for the given conversion.

Table 3



Scheme 2. Tentative mechanism for reduction of D-mannose to D-mannitol.

D-mannitol selectivity decreased continuously on increasing the catalyst ratio from 5.0 to 6.25 wt%. For highest yield D-mannitol, the catalyst ratio on initial D-mannose is found to be sufficient in between 5.0 wt%.

#### 3.5. Deactivation of catalysts

The reusability of the catalyst is of great importance for commercial feasibility; therefore, a set of four successive experiments were carried out for the possibility of reusing it. At the end of the first experiment the separated catalyst was fed into the reaction flask and the procedure was repeated for three times. Each filtrate from these experiments was analyzed directly for D-mannitol content. The results of these experiments are tabulated in Table 4. The results of this table show that the deactivation of the catalyst is slow due to leaching of less content of Ni as well as Ru metals and



**Fig. 9.** Effect of time on D-mannose hydrogenation; catalyst = 1.0 g, D-mannose = 10 wt%, temp. =  $120 \degree C$ , impeller speed =  $1200 \ rpm$ , hydrogen (H<sub>2</sub>) pressure = 55 bar.



Fig. 10. Effect of catalyst ratio on D-mannose hydrogenation; D-mannose = 10 wt%, temp. =  $120 \,^{\circ}$ C, time = 240 min, impeller speed = 1200 rpm, hydrogen (H<sub>2</sub>) pressure = 55 bar.

can be used several times with only marginal effect on D-mannose conversion, yield and selectivity to D-mannitol. This is because Dmannitol like D-sorbitol has a little effect on the activity of the catalyst as explained by Pijnenburg et al. [36]. They found that both D-sorbitol and D-mannitol had a little effect on the activity of the catalyst.

#### Table 4

Deactivation of NiO-TiO $_2$  supported ruthenium catalyst and leaching (mg/L) of metals.

Experiment no.	Mannose (%conversion)	D-mannitol (%selectivity)	D-mannitol (%yield)	Ru	Ti	Ni
1	97.4	93.6	91.2	0.0	N.D	11.1
2	96.4	92.3	89.0	0.0	N.D.	12.0
3	95.3	92.3	88.0	0.1	N.D.	13.5
4	92.3	92.0	84.9	0.3	N.D.	14.5

#### 4. Conclusions

NiO-modified TiO<sub>2</sub> support ruthenium catalyst is successfully prepared by impregnation method. In the Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub> catalyst, ruthenium is highly dispersed over a new class of NiO-modified TiO<sub>2</sub> (NiO-TiO<sub>2</sub>) support. The hydrogenation of pmannose to mannitol using Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub> catalyst is of first order with respect to D-mannose concentration. The activation energy for hydrogenation of *p*-mannose is low indicating catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub> is active for D-mannose hydrogenation. The catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub> is very stable and can be used several times with only a small decrease of D-mannitol yield. Optimized reaction conditions allowing maximum conversion of D-mannose as well as maximum yield and selectivity to D-mannitol were as follows; 1.0 g of catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub>, at impeller speed of 1200 rpm, at temperature of 120 °C and at hydrogen H<sub>2</sub> pressure of 55 bar for 240 min. Overall, it is concluded that the novel catalyst Ru (1.0%)/NiO (5.0%)-TiO<sub>2</sub> can be used for all industrial applications in hydrogenation of carbohydrate sugar to sugar alcohols.

#### Acknowledgements

This work was supported by the Institutional Research Program of KRICT (SI-1201) and by a grant (B551179-10-03-00) from the cooperative R&D Program funded by the Korea Research Council Industrial Science and Technology, Republic of Korea.

#### References

- B.W. Hoffer, E. Crezee, F. Devred, P.R.M. Mooijman, W.G. Sloof, P.J. Kooyman, A.D. van Langeveld, F. Kapteijn, J.A. Moulijn, Appl. Catal. A: Gen. 253 (2003) 437–452.
- P. Gallezot, P.J. Cerino, B. Blanc, G. Flèche, P. Fuertes, J. Catal. 146 (1994)93–102.
   P.J. Cerino, G. Fleche, P. Gallezot, J.P. Salome, Stud. Surf. Sci. Catal. 59 (1991)
- 231–236.
- [4] H. Li, W. Wang, J.F. Deng, J. Catal. 191 (2000) 257–260.
- [5] S. Schimpf, C. Louis, P. Claus, Appl. Catal. A: Gen. 318 (2007) 45-53.

- [6] N. Déchamp, A. Gamez, A. Perrard, P. Gallezot, Catal. Today 24 (1995) 29–34.
   [7] J.-P. Mikkola, H. Vainio, T. Salmi, R. Sjöholm, T. Ollonqvist, J. Väyrynen, Appl.
- Catal. A: Gen. 196 (2000) 143–155. [8] B. Kusserow, S. Schimpf, P. Claus, Adv. Synth. Catal. 345 (2003) 289–299.
- [9] B.W. Hoffer, E. Crezee, P.R.M. Mooijman, A.D. van Langeveld, F. Kapteijn, J.A.
- Moulijn, Catal. Today 79–80 (2003) 35–41. [10] K. van Gorp, E. Boerman, C.V. Cavenaghi, P.H. Berben, Catal. Today 52 (1999)
- 349–361. [11] D.K. Mishra, J.-M. Lee, J.-S. Chang, J.-S. Hwang, Catal. Today 185 (2012) 104–108.
- [12] E. Crezee, B.W. Hoffer, R.J. Berger, M. Makkee, F. Kapteijn, J.A. Moulijn, Appl.
- Catal. A: Gen. 251 (2003) 1–17. [13] H. Guo, H. Li, J. Zhu, W. Ye, M. Qiao, W. Dai, J. Mol. Catal. A: Chem. 200 (2003)
- 213-221.
- [14] H. Guo, H. Li, Y. Xu, M. Wang, Mater. Lett. 57 (2002) 392–398.
- [15] A. Perrard, P. Gallezot, J.-P. Joly, R. Durand, C. Baljou, B. Coq, P. Trens, Appl. Catal. A: Gen. 331 (2007) 100–104.
- [16] M. Yadav, D.K. Mishra, J.-S. Hwang, Appl. Catal. A: Gen. 425–426 (2012) 110–116.
- [17] J. Kuusisto, J.-P. Mikkola, M. Sparv, J. Wärnå, H. Karhu, T. Salmi, Chem. Eng. J. 139 (2008) 69–77.
- [18] B. Toukoniitty, J. Kuusisto, J.P. Mikkola, T. Salmi, D.Yu. Murzin, Ind. Eng. Chem. Res. 44 (2005) 9370–9375.
- [19] J. Kuusisto, J.P. Mikkola, P.P. Casal, H. Karhu, J. Vayrynen, T. Salmi, Chem. Eng. J. 115 (2005) 93-102.
- [20] H.W. Wisselink, R.A. Weusthuis, G. Eggink, J. Hugenholtz, G.J. Grobben, Int. Diary J. 12 (2002) 151–161.
- [21] F.N.W. von Weymarn, K.J. Kiviharju, S.T. Jaaskelainen, M.S.A. Leisola, Biotechnol. Prog. 19 (2003) 815–821.
- [22] W. Soetaert, P.T. Vanhooren, E.J. Vandamme, Methods Biotechnol. 10 (1999) 261–275.
- [23] T.T. Ikawa, T. Watanabe, K. Nisizawa, Plant Cell Physiol. 13 (1972) 1017-1027.
- [24] J.M.H. Stoop, J.D. Williamson, D.M. Pharr, Trends Plant Sci. 5 (1996) 139-144.
- [25] J.B.W. Hammond, R. Nichols, J. Gen. Microbiol. 93 (1976) 309-320.
- [26] Z. Bano, S. Rajarathnam, Crit. Rev. Food Sci. Nutr. 27 (1988) 87–158.
- [27] J.-L. Mau, C.-C. Chyau, J.-Y. Li, Y.-H Tseng, J. Agric. Food Chem. 45 (1997) 4726-4729.
- [28] A.W. Heinen, J.A. Peters, H. van Bekkum, Carbohydr. Res. 328 (2000) 449-457.
- [29] M. Makkee, A.P.G. Kieboom, H. van Bekkum, Starch 37 (1985) 136–141.
- [30] J. Wisnlak, R. Simon, Ind. Eng. Chem. Prod. Res. Dev. 18 (1979) 50-57.
- [31] M. Takemura, M. Iijima, Y. Tateno, Y. Osada, H. Maruyama, US Patent 4083881, 11.4.1978.
- [32] J. Zhang, L. Lin, J. Zhang, J. Shi, Carbohydr. Res. 346 (2011) 1327–1332.
- [33] J.T. Richardson, R. Scates, M.V. Twigg, Appl. Catal. A 246 (2003) 137-150.
- [34] A.K. Coker, Modeling of Chemical Kinetics and Reactor Design, Gulf Publishing Company, Houston, 2001.
- [35] T. Furusawa, J.M. Smith, AIChE J. 20 (1974) 88.
- [36] H.C.M. Pijnenburg, B.F.M. Kuster, H.S. van der Baan, Starch 30 (1978) 352-355.