Applied Catalysis A: General 425–426 (2012) 110–116

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Catalytic hydrogenation of xylose to xylitol using ruthenium catalyst on NiO modified TiO_2 support

Mithilesh Yadav, Dinesh Kumar Mishra, Jin-Soo Hwang*

Biorefinery Research Center, Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Republic of Korea

ARTICLE INFO

Article history:
Received 13 September 2011
Received in revised form 2 March 2012
Accepted 3 March 2012
Available online 11 March 2012

Keywords:
Hydrogenation
Xylose
Xylitol
Ruthenium
NiO modified TiO_2 support

ABSTRACT

The activity of Ru catalyst on a new class of NiO modified TiO_2 support, Ru/(NiO–TiO_2), was studied in the liquid phase catalytic hydrogenation of xylose to xylitol. The TiO_2 support was modified by simple impregnation method using nickel chloride precursor and subsequent oxidation. Various catalysts with different targeted compositions of Ru (1.0 and 5.0 wt%) and NiO (1.0, 5.0 and 10 wt%) in NiO–TiO_2 were prepared. These catalysts were characterized by using energy dispersive X-ray analysis (EDX/EDS), temperature-programmed reduction (TPR), inductively coupled plasma (ICP) mass spectrometry, transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and CO chemisorption. The novel catalysts are evaluated for selective hydrogenation of xylose and the results compared with those obtained from conventional Raney Ni, Ru/C and Ru/TiO_2 catalysts carried out under identical reaction conditions. The effect of NiO additive in the catalyst Ru/(NiO–TiO_2), clearly found to enhance the conversion, yield and selectivity to xylitol. Furthermore, the order of catalytic activity may be given as Ru (1.0%)/NiO (5.0%)–TiO_2 > Ru (1.0%)/TiO_2 > Ru (1.0%)/C> Raney Ni. The effects of Ru and NiO loading, xylose concentration (2.5, 15 and 30 wt%) and temperature (100, 120 and 140 °C) were studied. Although at higher temp 140 °C, the conversion of xylose was increased to optimum level, xylose to xylitol selectivity decreased due to formation of by-products.

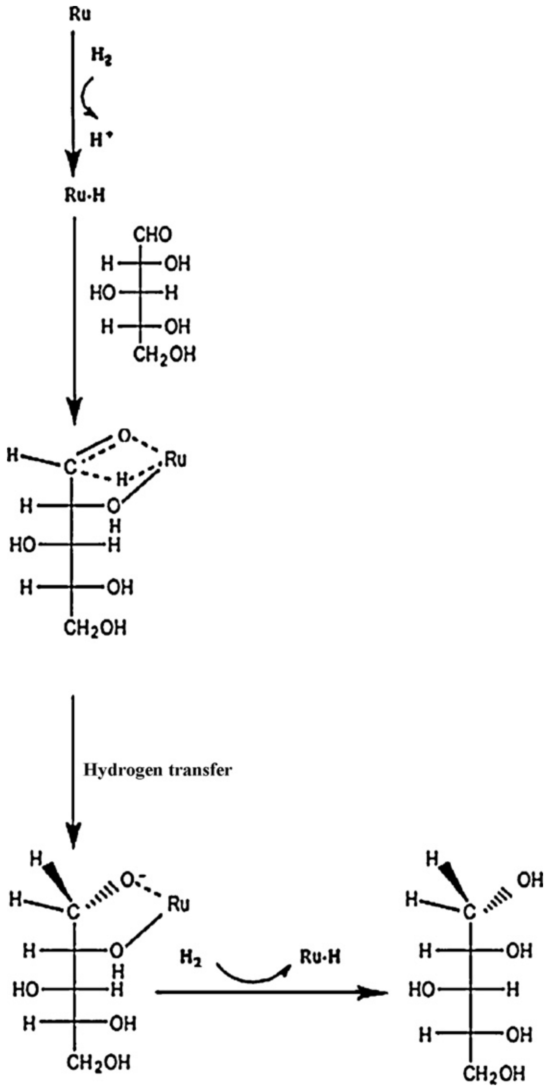
1. Introduction

The selective catalytic hydrogenation of naturally occurring sugar molecules to their corresponding sugar alcohols is an environment friendly route for the production of alternative sweeteners: solid metal-based catalysts are used in an aqueous environment and the hydrogen addition is brought about through catalytic reactions, thus avoiding the use of stoichiometric reducing agents and the subsequent formation of inorganic salts as waste material [1–3]. Xylitol, a penta carbon sugar alcohol with interesting properties, is an excellent artificial sweetener gaining large importance in recent years. The annual xylitol market is estimated to be around \$340 million priced at ~\$5/kg indicating its significance in many food and other value added chemical industries. It is highly soluble in water, does not caramelize at elevated temperatures, its sweetening capacity exceeds that of sugar and has lower insulin requirements, thus being especially suitable for usage by diabetics. Over the last few years, the demand for xylitol has increased enormously [4–7]. Xylitol also finds applications in several other industries such as in pharmaceutical, cosmetic, and synthetic resin [8–11]. The hydrogenation of xylose to xylitol is traditionally carried out in a three-phase slurry batch reactor over Raney nickel catalysts [12]. The principal advantages of the use of nickel catalysts are its lower price, ease of use as suspended slurry in typical batch reactions, good activity and selectivity [11,13]. Nevertheless, the major drawback of Raney Ni catalysts, usually, is their relatively fast deactivation due to accumulation of organic impurities (from the starting material) on the catalyst surface, leading to poisoning of the active sites, and metal leaching [1,14–16]. Consequently, conversion rates and process selectivity are jeopardized. In addition, it is most important that Ni must be completely removed from hydrogenated xylitol solution when it is used in the food industry, or as medicine or cosmetics, which adds further costs since expensive purification steps such as ion-exchange, filtering and crystallization are involved [15]. The past few years have seen a variety noble (Pt, Pd, Ru) metals with some supports, but among them Ruthenium based catalysts which show much less or no deactivation, have been found as alternative to Ni based catalysts for hydrogenation processes in recent years [17–21]. Investigations are under progress for proper metal-support systems for the direct hydrogenation of xylose-rich solutions (Scheme 1) leading to high activity and selectivity levels towards xylitol production, while being less sensitive to the deactivation of catalyst surface by fouling species. Although some reports are available on the applications of Ru on activated carbon and TiO_2 support, there is no systematic study using modified TiO_2 support.

---

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

0926-860X/\$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.03.007



Scheme 1. Mechanism of reduction of xylose.

In the present investigation, a new class of NiO modified TiO_2, (NiO–TiO_2), supports are prepared by simple impregnation method using nickel chloride precursor salt and subsequent oxidation. Various ruthenium catalysts of intended compositions are further prepared by re-impregnating these NiO modified supports in aqueous solution of hydrated ruthenium (III) chloride. The novel catalysts are evaluated for liquid phase hydrogenation of xylose and the results obtained are presented and discussed with conventional Raney Ni, Ru (1.0%)/C & Ru (1.0%)/TiO_2 catalysts carried out under identical reaction conditions.

2. Experimental

2.1. Materials

Hydrated ruthenium (III) chloride ($RuCl_3 \cdot xH_2O$) was purchased from Strem Chemicals, Newburyport, MA01950 (USA). The nickel chloride, xylose and xylitol were purchased from Sigma–Aldrich company, Inc., USA. The supports titanium (IV) oxide (rutile type) (TiO_2), purity – 99.9%, shape fine powder ca. 1–2 micron purchased from Degussa and active carbon (C) from Sigma–Aldrich company, Inc., (USA) are used after drying at 110 °C. Raney Nickel (50% slurry in water, active catalyst), pore size (~50 μ), surface area (80–100 m^2/g) was purchased from Aldrich Chemical company, Inc., USA and used as such. De-ionized water was used as solvent for making all solutions.

2.2. Catalyst Ru/(NiO–TiO_2) preparation

The preparation of catalyst, Ru/(NiO–TiO_2), was carried out by impregnation method using ruthenium (III) chloride hydrate and new class of support, NiO modified TiO_2. The proposed novel support material, was prepared by the following procedure: required amount (4.8 g) of TiO_2 was immersed into aqueous solution nickel chloride (0.55 g) 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_2 support (NiO–TiO_2). The calculated amount of (NiO–TiO_2), was further re-impregnated with aqueous solution of ruthenium (III) chloride hydrate (0.52 g) and was kept in an oven at 110 °C overnight. The catalyst Ru/(NiO–TiO_2) thus prepared was reduced in a continuous flow of (5.0%) H_2/Ar at 200 °C for 3 h and then used immediately for the hydrogenation reactions. The catalysts Ru (1.0%)/C and Ru (1.0%)/TiO_2 were also prepared by abovementioned impregnation method.

2.3. Liquid phase hydrogenation of xylose

The hydrogenation experiments of xylose were conducted in a 200 mL SS autoclave. The catalyst was screened with xylose solution (20 wt%) prepared in water at approximately (60–65 °C). The hydrogen gas was purged into the reactor at 2.0 MPa H_2 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 1200 rpm impeller speed and 120 °C for 120 min at 5.5 MPa. The product components were 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_2 adsorption–desorption at 77 K 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 77 K with N_2 gas at relative pressures (P/P0) 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_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

Table 1
Catalytic activity of different Ru & Raney Ni catalysts.

Catalysts	% Conc.	Xylitol		Arabinitol		NI
		% Selc.	% Yield	% Selc.	% Yield	
Ru (1.0%)/NiO (5.0%)–TiO_2	99.9	99.8	99.7	0.1	0.1	0.0
Ru (1.0%)/TiO_2	97.1	99.0	96.1	0.1	0.1	1.0
Ru (1.0%)/C	96.5	97.5	94.0	0.2	0.2	2.3
Raney Ni	96.9	96.7	93.7	1.0	0.9	2.4

NI: not identified.

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.

3. Results and discussion

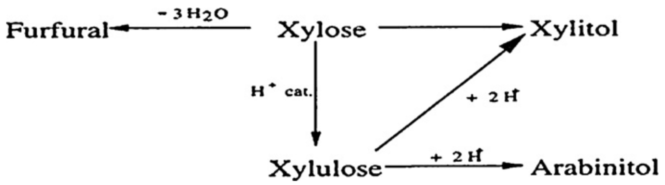
Novel Ru catalysts were prepared by simple impregnation method and characterized for their physico-chemical properties. The Ru loading in the catalysts were estimated by EDX and their leaching properties examined. The novel catalysts were evaluated for liquid phase hydrogenation of xylose and the results compared with those obtained from conventional Raney Ni, Ru (1.0%)/C and Ru (1.0%)/TiO_2 catalysts carried out under identical reaction conditions. The effects of varying metal content and NiO loading, xylose concentration and temperature were studied. The results obtained from these studies are presented and discussed below.

3.1. Liquid phase hydrogenation of xylose

Liquid phase catalytic hydrogenation of xylose, in principle, is simple but the formation of small amounts of by-products e.g. xylulose (through isomerization) complicates the process since xylulose may be hydrogenated further to arabinitol and xylitol (Scheme 2). In some cases under severe conditions, (at high temperatures and high concentrations of alkali) there is a possibility of formation of furfural and xylonic acid as by-products. It is known that alkali-catalyzed Cannizzaro reaction is normally responsible for formation of xylonic acid. In general, the reaction conditions are chosen in such a way that the formation of xylonic acid and furfural is prohibited. Thus the main by-products are xylulose and arabinitol and their generation is suppressed by using low temperature and high hydrogen pressure [22], which is not realistic in many catalytic hydrogenation processes practiced. As mentioned in the experimental section, the hydrogenated product was analyzed using HPLC technique using Sugar-Pak column and RI detector and typical HPLC chromatogram obtained is shown in Fig. 1. As anticipated the main peak due to xylitol and very small fractions of arabinitol, xylose and furfural are explicitly seen in the chromatogram.

The catalytic activity of novel Ru catalysts prepared was studied for liquid phase hydrogenation of xylose; results are presented in Table 1. Reactions carried out under identical conditions using Raney Ni & other Ru catalysts are included in the table for comparative purposes. The results, characteristically, indicate higher selectivity of all Ru catalysts [Ru/C, Ru/TiO_2 and Ru/(NiO–TiO_2)] compared to conventional Raney Ni catalyst due to higher reactivity of Ru than Ni. It is also seen from the table that values of conversion of xylose, yield and selectivity to xylitol with respect to Ru (1.0%)/TiO_2 are higher than those obtained with Ru (1.0%)/C. Most importantly, the novel catalyst prepared in this study [Ru (1.0%)/NiO (5.0%)–TiO_2], distinctively showed optimum conversion of xylose (99.9%) with the yield (99.7%) and the selectivity to xylitol (99.8%). Based on the above results, the order of catalytic activity (with reference to selectivity) may be given as Ru (1.0%)/NiO (5.0%)–TiO_2 > Ru (1.0%)/TiO_2 > Ru (1.0%)/C > Raney Ni.

The physico-chemical properties of the two Ru catalysts prepared were characterized using various methods and the values are given in Table 2



Scheme 2. Main and side reactions in xylose hydrogenation.

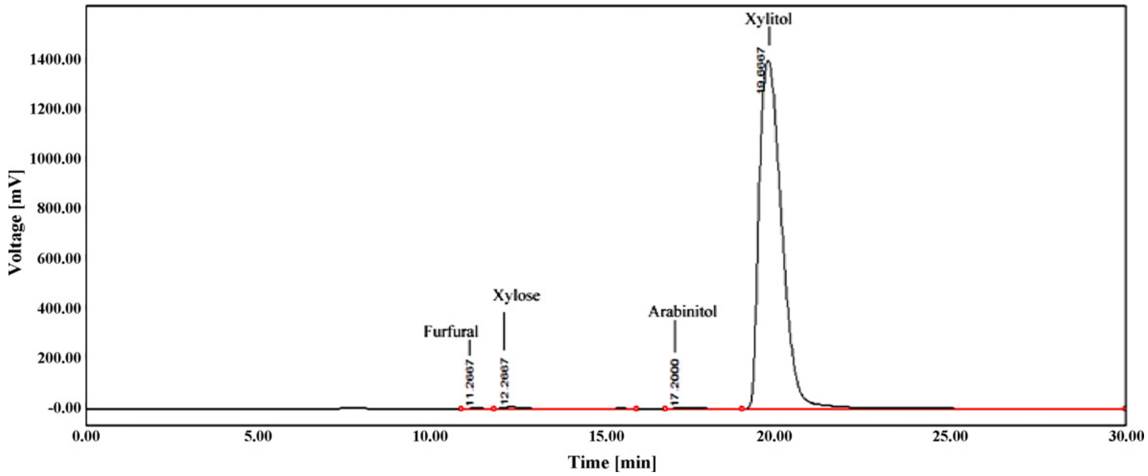


Fig. 1. A typical HPLC chromatogram of hydrogenated products, Reaction conditions: [xylose] = 20 wt%, temperature = 120 °C, time = 120 min, pressure = 5.5 MPa, stirring speed = 1200 rpm.

Table 2
Characteristic properties of the catalysts Ru (1.0%)/NiO (5.0%)–TiO_2 and Ru (1.0%)/TiO_2.

Catalysts	Precursors	S_{BET}[a] (m^2/g)	[$V_{micro\ pore}$[a]] × 10^2 (cm^3/g)	S_{Ru}[b] (m^2/g catalyst)	Dispersion[b] (%)	Particle size[c] (nm)
Ru (1.0%)/NiO (5.0%)–TiO_2[d]	($RuCl_3 \cdot xH_2O$)	42.5	0.31	1.9	63.2	2.0
Ru (1.0%)/TiO_2[d]	–	57.6	0.43	4.3	97.8	2.5

[a] Determined by N_2 adsorption–desorption at 77 K.
[b] Determined by CO adsorption–desorption.
[c] Obtained by transmission electron microscopy (TEM).
[d] Reduction with a continuous flow of H_2/Ar (5.0%) at 200 °C.

Table 3
Ruthenium content and study of leaching property.

Catalysts	Precursors	Ru content[a] (wt%)	Ru loading[b] (wt%)	Leaching[c] (mg/L)		
				Ru	Ti	Ni
Ru (1.0%)/NiO(5.0%)–TiO_2[d]	($RuCl_3 \cdot xH_2O$)	1.0	1.2	0.31	N.D.	11.0
Ru (1.0%)/TiO_2[d]	–	1.0	0.9	0.34	N.D.	0.0

[a] Ru content (1.0 wt%) loaded on NiO modified TiO_2 support experimentally.
[b] Obtained by energy dispersive X-ray (EDX) analysis.
[c] Obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES).
[d] Reduction with a continuous flow of H_2/Ar (5.0%) at 200 °C.

Table 4
The effect of ruthenium and NiO (%) loading on the conversion of xylose, yield and selectivity to xylitol.

Catalysts of ruthenium on NiO modified TiO_2 support		% Conv.	Xylitol		Arabinitol		NI
Ru (%)	NiO (%)		% Selc.	% Yield	% Selc.	% Yield	% Selc.
1.0	1.0	98.8	98.8	98.1	0.2	0.2	0.5
1.0	5.0	99.9	99.8	99.7	0.1	0.1	0.0
1.0	10	98.4	98.4	97.1	0.3	0.3	1.1
5.0	5.0	100	100	99.8	0.1	0.1	0.0

NI: not identified.

. It is clear from the table that, although the dispersion of Ru on (NiO–TiO_2) support and the S_{BET} are lower than that of Ru (1.0%)/TiO_2, the catalyst Ru (1.0%)/NiO (5.0%)–TiO_2 demonstrated excellent results towards selective hydrogenation of xylose to xylitol. The lower values of dispersion may be attributed due to slightly higher loading of Ru metal (1.2% compared to 0.9%) in Ru (1.0%)/NiO (5.0%)–TiO_2 causing aggregation of particles.

The leaching properties of the two Ru catalysts Ru (1.0)/TiO_2, Ru (1.0%)/NiO (5.0%)–TiO_2 were examined by analyzing the product solutions; details of the methods used and the results are summarized in Table 3. The extent of Ru metal leaching in modified catalyst was observed to be lower than Ru (1.0%)/TiO_2 thus, signifying its better stability.

3.2. The effect of ruthenium and NiO (%) loading

As mentioned earlier, catalysts with different targeted compositions [Ru (1.0 and 5.0 wt%) and NiO (1.0, 5.0 and 10 wt%)] were used to study their effects on hydrogenation of xylose and observed results are given in Table 4. The first three entries refer to experiments with constant (1.0 wt%) Ru and varying NiO (1.0, 5.0 and 10 wt%). It is seen from the table that low values of conversion of xylose, yield and selectivity to xylitol 98.8%, 98.1% and 98.8%, respectively, are observed with (1.0 wt%) NiO and attributed to formation of ~0.2% arabinitol as by-products. The values increased to their optimum with (5.0 wt%) NiO in the catalyst [conversion (98.8–99.9%), yield (98.1–99.7%) and the selectivity to xylitol (98.8–99.8%)] by minimizing the formation of arabinitol and other by-products. However, with further increasing of NiO to 10 wt% the values decreased may be due to formation of large amount of arabinitol and other by-products.

The second and fourth entries (Table 4) refer to experiments with constant (5.0 wt%) NiO and varying Ru (1.0 and 5.0 wt%) in the catalyst. It is observed that there is negligible increase in the values of conversion of xylose (99.9–100%), yield (99.7–99.8%) and selectivity to xylitol (99.9–100%). Although the above values catalyzed by 5.0 wt% Ru in the catalyst sample are highest, incorporation of 1.0 wt% Ru is more than enough for all practical purposes as metal Ru is expensive.

Based on the above results, it may be stated that 1.0 wt% Ru and 5.0 wt% NiO in the catalyst i.e. the catalyst [Ru (1.0%)/NiO (5.0%)–TiO_2] is capable enough to produce the best possible values of conversion of xylose, yield and selectivity to xylitol.

3.3. Effect of xylose concentrations and temperatures

As the combination of 1.0 wt% Ru and 5.0 wt% NiO in the catalyst, [Ru (1.0%)/NiO (5.0%)–TiO_2], showed better activity and hence was employed to study the influence of xylose concentration and temperature on hydrogenation of xylose. The influence of xylose concentration was studied by carrying out the reaction using three different concentrations ranging from 2.5 to 30 wt% and the results are shown in Fig. 2. With 2.5 wt%, the results explicitly show that the conversion of xylose and selectivity to xylitol is highest (100%). Strong adsorption of xylose molecules during hydrogenation reaction is speculated for the optimum values observed. However, it is noticed that with further increase in xylose concentration (15–30 wt%), the xylose conversion decreased continuously to 96.6%. The low conversions observed may be due to relatively weak adsorption of xylose molecules at higher xylose concentrations [23,24].

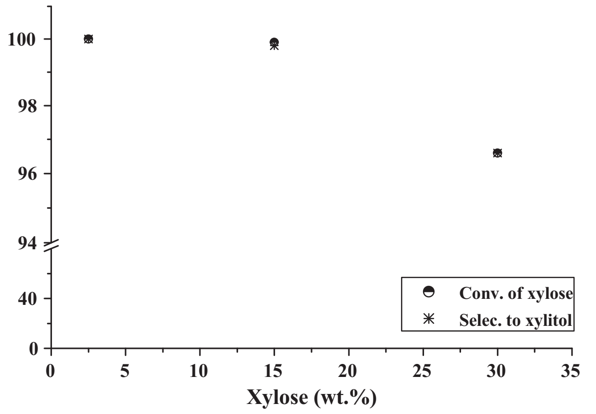


Fig. 2. The effect of xylose concentration on the conversion of xylose and the selectivity to xylitol.

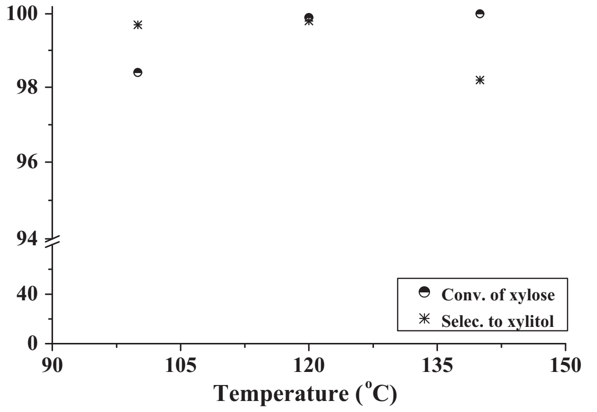


Fig. 3. The effect of temperature on the conversion of xylose and the selectivity to xylitol.

The effect of temperature on hydrogenation of xylose was studied by varying the reaction temperature from 100 to 140 °C and the results are shown in Fig. 3 where both conversion and the selectivity values are plotted against reaction temperature. It is seen from the figure that the xylose conversion increased gradually in the investigated temperature range. This may be due to the fact that the activity of NiO modified TiO_2 support to cleave C–O bond was obviously increased with increasing reaction temperature [25,26]. It is clear from the figure that the optimum reaction temperature lies very close to 120 °C as both conversion and selectivity values are nearer to 100%. On further increasing the temperature to 140 °C, it is evident that although the conversion of xylose reached 100%, the selectivity to xylitol decreased since it is known that higher the temperature, the more prominent is formation of by-products [arabinitol (0.5%) and other by-products (1.3%)] [27].

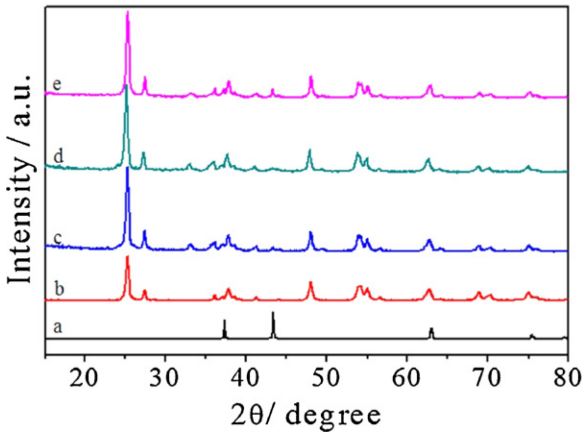


Fig. 4. XRD profile of NiO (shown for reference peaks) (a), TiO_2 (b), (NiO–TiO_2) (c), Ru (1.0%)/NiO (5.0%)–TiO_2 (fresh sample) (d), and Ru (1.0%)/NiO (5.0%)–TiO_2 (after hydrogenation) (e).

3.4. Characteristic properties of the catalyst

The X-ray diffraction patterns of neat NiO (a); given as for reference, neat TiO_2 (b), modified NiO–TiO_2 (c), catalyst Ru/(NiO–TiO_2) (d) and catalyst Ru (1.0%)/NiO (5.0%)–TiO_2 (after hydrogenation) (e) are shown in Fig. 4. It is seen from this figure that the XRD profiles of TiO_2 support (b: red colour) and NiO modified TiO_2 support (c: blue colour) have obvious differences. The presence of characteristics NiO peaks (in profile c) which appeared at 2θ values of 37°, 43°, 62°, 75° and 79° indicate successful modification of TiO_2 support with nickel chloride. In addition, the XRD profiles of NiO–TiO_2 (c, blue color) and its catalyst of Ru (d, green color) look alike. The metallic Ru in the catalyst could not be detected as Ru loadings less than 5.0% are always covered by NiO modified TiO_2 support making it difficult to determine [28]. The XRD profile of fresh catalyst sample i.e. before hydrogenation Ru/(NiO–TiO_2) (d: green color) and after hydrogenation (e: pink color) unambiguously demonstrates that the catalyst is absolutely stable during hydrogenation reaction.

Fig. 5 presents TEM images of the catalysts Ru (1.0%)/TiO_2 and [Ru (1.0%)/NiO (5.0%)–TiO_2]. The dark portion of the image (Fig. 5a)

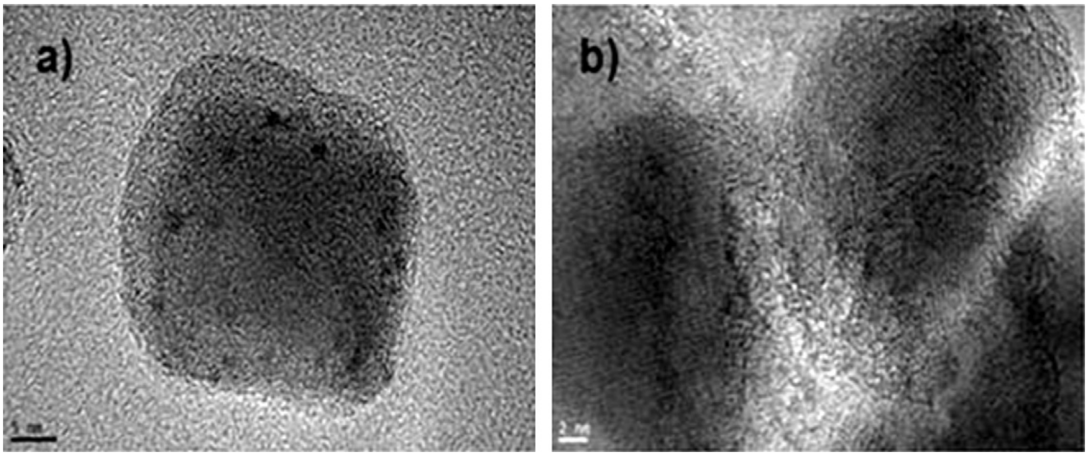


Fig. 5. TEM images of the catalysts Ru (1.0%)/TiO_2 (a) and Ru (1.0%)/NiO (5.0%)–TiO_2 (b).

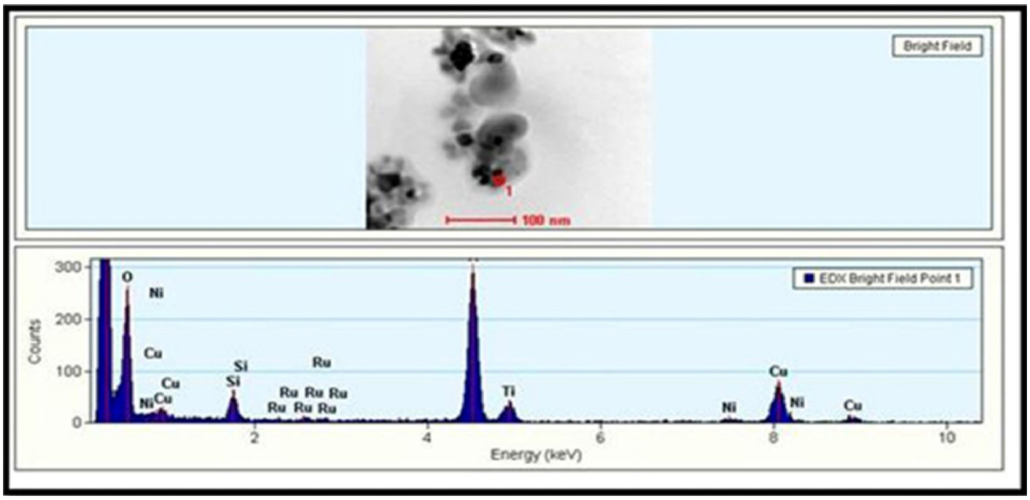


Fig. 6. EDX spectrum of the catalyst Ru (1.0%)/NiO (5.0%)–TiO_2.

reveal the presence of particles of size ~2.5 nm, which correspond to the Ru particles dispersed on large flakes (gray portion) of TiO_2 support. Whereas, Fig. 5(b) displays the particles with slightly higher size range from 10 to 12 nm corresponding to NiO particles interacted with TiO_2 support. However, the presence of Ru particles though they are present along with NiO particles on the NiO–TiO_2 support could not be identified clearly. In order to confirm their presence EDX analysis was carried out and the spectrum is presented in Fig. 6. The spectrum undoubtedly shows the presence of all three components Ru, Ni and Ti of the catalyst [Ru (1.0%)/NiO (5.0%)–TiO_2].

The reducibility of the catalysts prepared was examined by TPR; the profiles of the catalysts Ru/TiO_2, NiO modified TiO_2 support, (NiO–TiO_2) and Ru/NiO–TiO_2 are shown in Fig. 7. Two TPR peaks observed at 170 °C and 320 °C in red profile (curve a) are attributed to the respective reduction of ruthenium chloride ($Ru^{3+} \rightarrow Ru^0$) and ($Ru^{4+} \rightarrow Ru^0$) oxidized ruthenium on TiO_2 surface. A main peak observed at 378 °C (in curve b) is due to conversion of Ni^{2+} to Ni^0, which is in accordance with Richardson et al. findings as NiO needs to reduce into Ni at higher temperature [29]. On the other hand, the profile of [Ru (1.0%)/NiO (5.0%)–TiO_2] (curve c) displayed a peak at 150 °C which is attributed to the reduction of $Ru^{3+} \rightarrow Ru^0$ and the second peak at 360 °C is due to the reduction of $Ni^{2+} \rightarrow Ni^0$. There is an additional peak observed at 425 °C which is attributed to delayed reduction of $Ni^{2+} \rightarrow Ni^0$. It is clear from the TPR data that a temperature of ~200 °C is enough for the reduction of $Ru^{3+} \rightarrow Ru^0$ without affecting the NiO modified TiO_2 support.

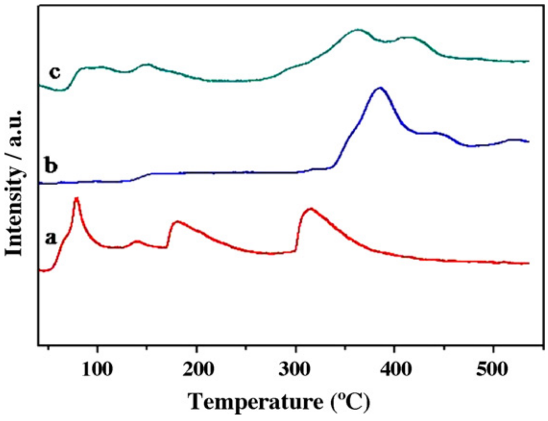


Fig. 7. H_2–TPR profile of Ru (1.0%)/TiO_2) (a), (NiO–TiO_2) (b) and Ru (1.0%)/NiO (5.0%)–TiO_2 (c).

4. Conclusions

Catalytic liquid phase hydrogenation of xylose to xylitol using a Ru catalyst on NiO modified TiO_2 support was examined. A variety of Ru catalysts with predetermined compositions were prepared and used to study the hydrogenation of xylose and the results compared with Ni and other Ru catalysts carried out under identical reaction conditions. The catalyst [Ru (1.0%)/NiO (5.0%)–TiO_2], unequivocally showed optimum conversion of xylose (99.9%) with the yield (99.7%) and the selectivity to xylitol (99.8%). The order of catalytic activity was observed to be [Ru (1.0%)/NiO (5.0%)–TiO_2] > [Ru (1.0%)/TiO_2] > [Ru (1.0%)/C] > [Raney Ni]. The percent NiO incorporated in modified support (NiO–TiO_2) played an important role to minimize arabinitol and other by-products, which generally form during hydrogenation of xylose. Although the values of conversion of xylose, yield and selectivity to xylitol with incorporation of 5.0 wt% Ru in the catalyst are maximum, the results obtained with 1.0% Ru are close to 100% and hence is more than enough for all industrial applications as metal Ru is expensive.

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

[1] P. Gallezot, N. Nicolaus, G.F. Lèche, P. Fuertes, A. Perrard, J. Catal. 180 (1998) 51–55.
[2] J.P. Mikkola, T. Salmi, R. Sjöholm, J. Chem. Technol. Biotechnol. 74 (1999) 655–662.
[3] J. Kuusisto, J.P. Mikkola, M. Sparv, J. Warna, H. Heikkila, R. Perala, J. Vayrynen, T. Salmi, Ind. Eng. Chem. Res. 45 (2006) 5900–5910.
[4] J.C. Parajó, H. Domínguez, J.M. Domínguez, Bioresour. Technol. 65 (1998) 191–201.
[5] J. Zhang, A. Geng, C. Yao, Y. Lu, Q. Li, Bioresour. Technol. 105 (2012) 134–141.
[6] G. Franceschin, M. Sudiro, T. Ingram, I. Smirnova, G. Brunner, A. Bertucco, Chem. Eng. Res. Des. 89 (2011) 631–664.
[7] Y. Zou, K. Qi, X. Chen, X. Miao, J.-J. Zhong, J. Biosci. Bioeng. 109 (2010) 149–152.
[8] J. Wisniak, M. Hershkowitz, S. Stein, Ind. Eng. Chem. Prod. Res. Develop. 13 (1974) 232–236.
[9] S.B. Kim, Y.Y Lee, Biotechnol. Bioeng. 15 (1985) 81–90.
[10] J.P. Mikkola, T. Salmi, Chem. Eng. Sci. 54 (1999) 1583–1588.
[11] J.P. Mikkola, T. Salmi, Catal. Today 64 (2001) 271–277.

[12] M. Herskowitz, Chem. Eng. Sci. 40 (1985) 1309–1311.
[13] K. van Gorp, E. Boerman, C.V. Cavenaghi, P.H. Berben, Catal. Today 52 (1999) 349–361.
[14] H. Funk, Appl. Polym. Symp. 28 (1975) 145–152.
[15] J.P. Mikkola, R. Sjöholm, T. Salmi, P. Mäki-Arvela, Catal. Today. 48 (1999) 73–81.
[16] H.M. Baudel, N.M. Lima, A. Knoechelmann, C.A.M. de Abreu, Proc. 7th Braz. Symp. Chem. Lignins Wood Components, Belo Horizonte, Brazil, 2001, pp. 401–405.
[17] B.S. Kwak, B.I. Lee, T.Y. Kim, J.W. Kim, WO Patent 2005/021475, 2005.
[18] D.C. Elliott, A.W., Todd, Y., Wang, J.G., Frye, Jr., US Patent 6235797, 2001.
[19] D. Vanoppen, M. Maas-Brunner, U. Kammel, J.D. Arndt, DE 10128205, 2002.
[20] H. Ling, K. Cheng, J. Ge, W. Ping, Nat. Biotechnol. 28 (2011) 673–678.
[21] W.Y. Jeon, B.H. Yoon, W.Y. Shim, J.H. Kim, J. Biotechnol. 150 (2010) 345–346.
[22] J.P. Mikkola, H. Vainio, T. Salmi, R. Sjöholm, T. Ollonqvist, J. Väyrynen, Appl. Catal. A: Gen. 196 (2000) 143–155.
[23] H. Guo, H. Li, J. Zhu, W. Ye, M. Qiao, W. Dai, J. Mol. Catal. A: Chem. 200 (2003) 213–221.
[24] J.-P. Mikkola, T. Salmi, R. Sjöholm, Stud. Surf. Sci. Catal. 122 (1999) 351–358.
[25] A. Tanksale, Y. Wong, J.N. Beltramamini, G.Q. Lu, Int. J. Hydrogen Energy 32 (2007) 717–724.
[26] F.C. Sampaio, C.A.D. Moraes, D.D. Faveri, P. Perego, A. Converti, F.M.L. Passos, Process Biochem. 41 (2006) 675–681.
[27] H. Hofmann, Chemie. Ing. Techn., in: M. Grayson (Ed.), Kirk-Othmer: Encyclopedia of Chemical Technology, 3rd ed., Wiley, New York, 1984, vol. 1, pp. 754–778, vol. 24, pp. 22–26.
[28] J. Zhang, L. Lin, J. Zhang, J. Shi, Carbohydr. Res. 346 (2011) 1327–1332.
[29] J.T. Richardson, R. Scates, M.V. Twigg, Appl. Catal. A. 246 (2003) 137–150.