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Hydrogenation of fructose over amorphous nano-catalysts of CoNiB and polymer-stabilized CoNiB

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ABSTRACT

Fructose and invert sugar (fructose/glucose mixture) were hydrogenated over bimetallic amorphous nano-catalysts of CoNiB and polymer polyvinylpyrrolidone (PVP)-stabilized CoNiB (PVP-CoNiB), prepared by chemical reduction, to yield mannitol and sorbitol. The parameters of catalysts and the reaction conditions were discussed. CoNiB and PVP-CoNiB catalysts were much more active than NiB, CoB and Raney nickel in the hydrogenations of fructose and invert sugar. The selectivity of mannitol changed slightly even as the catalysts and the reaction conditions were altered. The highly active catalysts of CoNiB and PVP-CoNiB are promising to replace Raney nickel in the hydrogenations of fructose and invert sugar, although the selectivity of mannitol improved slightly.

1. Introduction

Mannitol, a six-carbon sugar alcohol, is naturally present in small amounts in many plants. Mannitol has a sweet cool taste with a relative sweetness of about 50% of that of sucrose. Mannitol, which has a low chemical reactivity; is non-toxic, non-hygroscopic and a low caloric sweetener, is extensively used in the food and pharmaceutical industries [1–5].

Mannitol can be produced by chemical and biological methods. The biological method suffers from a low volumetric productivity [5–6]. At present, mannitol is produced industrially by the catalytic hydrogenation of fructose or syrups (mixtures of glucose and fructose) at high pressure and a high temperature, with sorbitol as the major by-product, as shown in Scheme 1 [1–6]. The industrial hydrogenation of invert sugar (glucose/fructose = 1/1, obtained by the hydrolysis of sucrose) over Raney nickel produces a mixture of mannitol and sorbitol in a weight ratio of about 25/75 [1,7]. The yield of mannitol from the hydrogenation of syrups can be increased by increasing the content of fructose, because the hydrogenation of glucose produced only sorbitol. Hydrogenation of pure fructose over general nickel-based catalysts gives mannitol selectivity and yields about 45–50% [3,7]. A higher selectivity of mannitol about 65% can be substantially obtained over copper-based catalysts of $Cu/ZnO/Al_2O_3$ and Cu/SiO_2, but such copper-based catalysts are much less active than the nickel-based catalysts [2].

Amorphous alloy catalysts of NiB and CoB, prepared by chemical reduction in aqueous solution with $NaBH_4$ or KBH_4 as the reducing agent [8–13], have been characterized by EXAFS as structures with long-range disorder and short-range order [12,13], and by TEM as nano-sized particles (20–50 nm). They exhibit greater activity, selectivity and resistance to sulfur-poisoning than general nickel and cobalt catalysts [9–19]. The catalytic properties of these nanoparticles are easily modified by introducing an extra metal or metal oxide [10,14,15]. Moreover, PVP-polymer stabilization method [20] has been recently employed with chemical reduction to yield highly dispersed NiB catalysts (3–5 nm), which are much more active than the conventional NiB catalyst in the hydrogenation reactions.

Bimetallic amorphous catalysts of CoNiB can also be prepared by chemical reduction, but they have not attracted as much attention as NiB and CoB. They have been used in the hydrogenation of benzene, sulfolene, acetonitrile and p-chloronitrobenzene [21–24], and they are more active than NiB and CoB. Recently, the authors systematically studied the preparation and catalytic properties of CoNiB and PVP-stabilized CoNiB catalysts [25]. The CoNiB catalysts exhibited much higher activity than NiB and CoB in the hydrogenation of unsaturated aldehydes, and the optimal molar ratio of Co/(Co + Ni) is about 0.5. CoNiBs are not physical mixtures of CoB and NiB, some interactions exist between Co and Ni in CoNiBs. Furthermore, the PVP-stabilized CoNiB catalysts are significantly more active than CoNiBs. In this work, the highly active nano-sized catalysts of CoNiB and PVP-CoNiB were used to replace the general commercial catalyst of Raney nickel for the hydrogenation of fructose and invert sugar. The parameters of catalysts and the reaction

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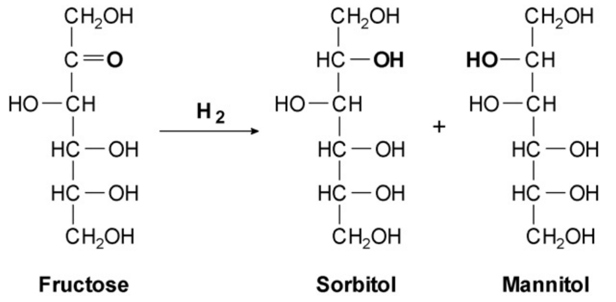

Scheme 1. Hydrogenation of fructose.

conditions were discussed in the hydrogenation of fructose and invert sugar.

2. Experimental

2.1. Preparation of catalyst

The CoNiB catalysts were prepared by reducing cobalt acetate and nickel acetate with sodium borohydride in aqueous solution at room temperature [25]. The composition of the samples was adjusted by changing the initial molar ratio Co/(Co + Ni) in the solution. Aqueous sodium borohydride (6 ml, 1 M) was added dropwise to the metallic salt solution (20 ml, 0.1 M) using a micropump in flowing nitrogen (40 ml/min). The resulting black precipitate was thoroughly washed four times with distilled water to remove residual ions. The fresh, wet catalysts were then ready to be used in the reaction. For characterization, the wet catalysts were first washed three times with ethanol to remove water, and were then dried and passivated at room temperature in a nitrogen stream that contained a trace of oxygen to enable characterization.

Polymer-stabilized CoNiB catalysts (PVP-CoNiB) were prepared by reducing cobalt acetate and nickel acetate (0.1 M) with sodium borohydride (1 M) in aqueous solution [20,25]. The water-soluble polymer of polyvinylpyrrolidone (PVP, MW 10,000) served as a protective reagent. Before reduction, an appropriate quantity of PVP was dissolved in the salt solution.

2.2. Characterization of catalyst

The specific surface areas (S_{BET}) of the samples were obtained by nitrogen adsorption with an ASAP 2010 apparatus at 77 K, following degassing at 373 K. The bulk compositions of the samples were identified by inductively coupled plasma analysis (ICP) on a JOBIN JY-24 device.

Transmission electron microscopy (TEM) photographs were taken with a JEOL JEM-2999FMII apparatus. Samples for TEM were prepared by placing a drop of a colloidal dispersion of catalyst in the solvent of isopropanol onto a perforated copper grid, followed by naturally evaporating the solvent. The mean particle diameters were calculated by counting ~100 particles from the enlarged photographs.

2.3. Reaction studies

A fresh, as-prepared catalyst was used in each reaction run. The hydrogenation of fructose or invert sugar was conducted in water (50 ml) using a magnetically stirred three-phase laboratory-scale autoclave (160 ml, Parr-4842). Normally, the hydrogenation of fructose over a CoNiB or PVP-CoNiB catalyst that contained 2 mmol of metals was conducted at 343 K and a constant pressure of 4 MPa. Notably, the amount of catalyst was small enough and the stirring rate of 500 rpm was fast enough to minimize the mass transfer resistance. The hydrogenation samples were analyzed after silylation [26–29] by gas chromatography with a fused silica capillary column of 30 m × 0.25 mm × 0.25 μm film thickness, attached to a flame ionization detector. No product other than mannitol and sorbitol was detected in each sample.

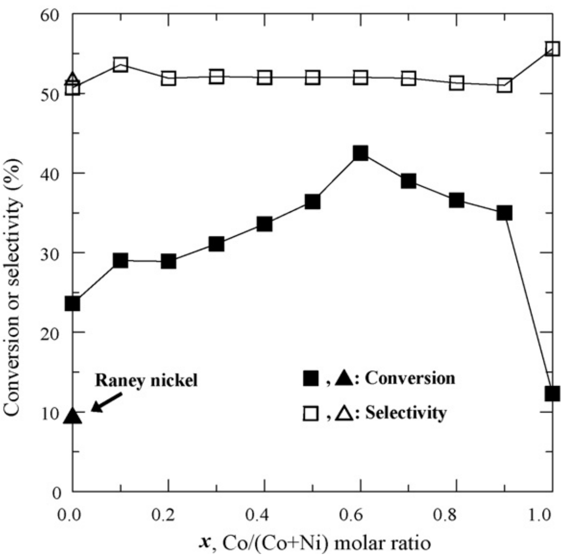

Fig. 1. Effect of the Co fraction in the CoNiB(x) catalysts on the fructose hydrogenation. Reaction conditions: T = 343 K; P = 4 MPa; fructose/water/metals in catalyst = 21.43 g/50 g/2 mmol; reaction time = 1 h.

The conversion and selectivity toward mannitol were calculated as follows:

$$\text{Conversion}(\%) = \frac{N_{F0} - N_F}{N_{F0}} \times 100$$

$$\text{Selectivity}(\%) = \frac{N_M}{N_M + N_S} \times 100$$

where N_{F0} is the initial moles of fructose in the feed; N_F, N_M and N_S represent the moles of fructose, mannitol and sorbitol in each sample, respectively.

3. Results and discussion

3.1. Preparation of catalysts

Bimetallic catalysts of CoNiB and PVP-CoNiB were prepared by chemical reduction. The hydrogenation of fructose was conducted at 343 K and 4 MPa, and the conversion for 1 h was adopted to examine the influence of the preparation parameters. As in a previous study [25], an adding rate of $NaBH_4$ solution of about 2 ml/min and a metal/$NaBH_4$ molar ratio of about 1/3 were optimal for preparing CoNiB catalysts. CoNiB(x) catalysts with various molar fractions of cobalt (x, Co/(Co + Ni) in molar ratio) were obtained by varying the ratio of precursor salts in the initial solution. Fig. 1 presents the hydrogenation of fructose over the CoNiB(x) catalysts. The conversions of fructose for 1 h increased with the cobalt fraction in CoNiB(x) up to 0.6, and the optimal catalyst CoNiB(0.6) was much more active than Raney nickel with about 4.4 times the conversion. The hydrogenation of fructose yielded sorbitol and mannitol, and the selectivity of mannitol was about 50%. The selectivity of mannitol only slightly changed with the cobalt fraction in CoNiB(x). The optimal cobalt ratio is larger than that (0.5) reported in the previous study on the hydrogenation of unsaturated aldehydes, which might change a little with the property of the reactant adsorbed on CoNiB(x).

The water-soluble polymer PVP with an average molecular weight of 10,000 was dissolved in the initial salt solution as a

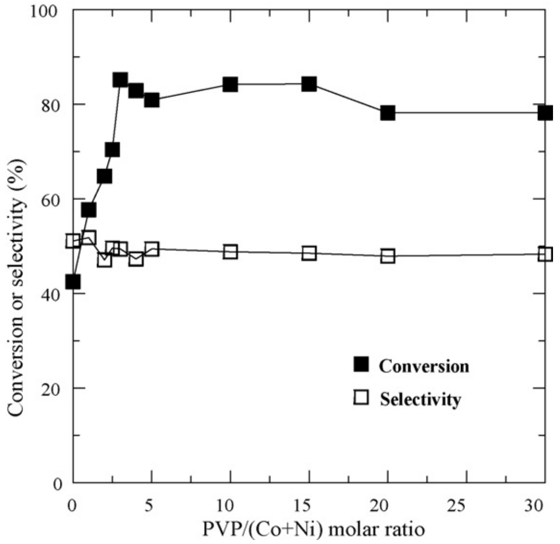

Fig. 2. Effect of PVP amount in the PVP-CoNiB(0.6) catalyst on the fructose hydrogenation.

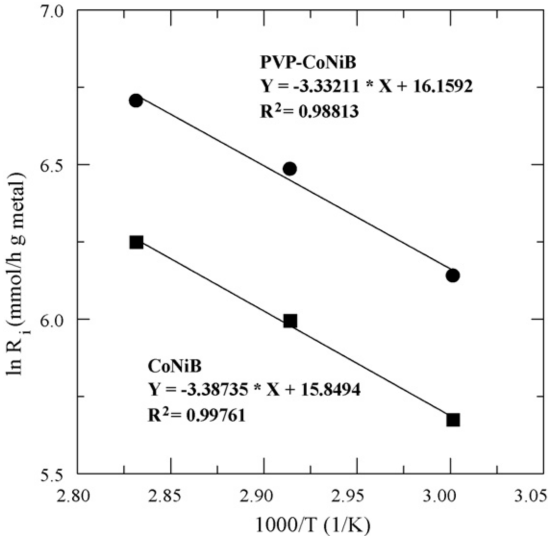

Fig. 3. Arrhenius plots for the hydrogenation of fructose over CoNiB and PVP-CoNiB catalysts.

protective reagent to prepare PVP-CoNiB(x) catalysts [25]. The optimal fraction of cobalt in the PVP-CoNiB(x) catalysts was also about 0.6, and the optimal molar ratio of PVP/metal in the initial solution was about 3, as shown in Fig. 2. The PVP(3)-CoNiB(0.6) catalyst was about twice as active as CoNiB(0.6). Maximum yields of mannitol of about 45% were obtained for both CoNiB(0.6) and PVP(3)-CoNiB(0.6) during the selective hydrogenation of fructose at 343 K and 4 MPa.

The physical properties of CoNiB and PVP-CoNiB catalysts were listed in Table 1. The molar ratios of cobalt in CoNiB and PVP-CoNiB were almost the same as those in the precursor solutions. The atomic ratios of metal/B in CoNiB and PVP-CoNiB were 2.2–2.5—almost the same as those of NiB and CoB. The specific surface areas of CoNiB decreased as the Co content increased, and that of PVP-CoNiB(0.6) was about double that of CoNiB(0.6). Undoubtedly, the water-soluble polymer PVP prevented the aggregation and growth of nanoparticles of CoNiBs. The particle sizes characterized by the TEM micrographs, as 4–7 nm for CoNiB and 3.5–6 nm for PVP-CoNiB, were more uniform and smaller than those of CoB and NiB.

The NiB ($x = 0$) catalyst was about twice as active as CoB ($x = 1$), and all of the CoNiB(x) catalysts were more active than NiB and CoB (Fig. 1). It was reconfirmed that the bimetallic catalyst of CoNiB is not just a physical mixture of NiB and CoB [25]. Furthermore, the conversions of fructose for 1 h increased with the cobalt fraction in CoNiB(x) up to 0.6 but the specific surface areas of CoNiB(x) decreased monotonously with the increases of cobalt fraction (Table 1), revealing that particle-size effect was not dominant in determining the activity of the hydrogenation of fructose over CoNiB catalysts. Some interaction occurred between Ni and Co in the CoNiB(x) catalysts, which affected the adsorption strength of the reactant on the catalyst. The carbonyl group is generally adsorbed by the negative dipole of oxygen in an end-on type, which adsorbed less strongly on nickel with more d-band electrons than on cobalt with fewer d-band electrons. The strength of adsorption of the carbonyl group on the CoNiB(x) catalysts increased as the d-band electron densities in the catalysts decreased, as the fraction of cobalt increased. This increase in adsorption strength of the carbonyl group on CoNiB(x) facilitated the hydrogenation of fructose up to a cobalt fraction of about 0.6. Clearly, the carbonyl group that was adsorbed on CoNiB(0.6) might have been in an optimal activated state for its reaction.

3.2. *Hydrogenation of fructose*

The effects of temperature, pressure and initial concentration of fructose on the hydrogenation rate were studied to optimize the hydrogenation of fructose to mannitol. Fructose was hydrogenated over CoNiB(0.6) and PVP(3)-CoNiB(0.6) at different temperatures in the range 333–373 K. The initial rate (R_i, mmol/h g_{metal}) increased with the temperature to around 353 K, with the maximal rates of 518 and 817 mmol/h g_{metal} for CoNiB(0.6) and PVP(3)-CoNiB(0.6), respectively. When the reaction temperature exceeded 353 K, the less competitive adsorption of hydrogen on the catalysts was unfavorable for the reaction. The plots of $\ln R_i$ versus $1/T$ in the range of 333–373 K (Fig. 3) yielded an apparent activation energy of about

Table 1
Conversions of fructose hydrogenation and bulk properties of CoNiB and PVP-CoNiB catalysts.

Catalyst	Conversion[c] (%)	Bulk composition (at. ratio)	Co/(Co + Ni) (molar ratio)	(Co + Ni)/B (at. ratio)	S_{BET} (m^2/g)	D (nm)
NiB	23.6	$Ni_{69.8}B_{30.2}$	0.000	2.3	27.9	7–15
CoNiB(0.4)[a]	33.6	$Co_{28.7}Ni_{42.4}B_{28.9}$	0.404	2.5	23.6	4–7
CoNiB(0.6)	42.5	$Co_{42.4}Ni_{28.3}B_{29.3}$	0.600	2.4	22.4	4–7
CoNiB(0.8)	36.6	$Co_{55.6}Ni_{14.1}B_{30.3}$	0.798	2.3	21.6	4–7
CoB	12.3	$Co_{69.2}B_{30.8}$	1.000	2.2	18.8	5–10
PVP(1)[b]-CoNiB(0.6)	57.7	$Co_{41.2}Ni_{27.6}B_{31.1}$	0.599	2.2	41.5	3.5–6
PVP(3)-CoNiB(0.6)	85.2	$Co_{42.3}Ni_{27.8}B_{29.9}$	0.603	2.3	42.9	3.5–6
PVP(5)-CoNiB(0.6)	80.9	$Co_{42.1}Ni_{28.0}B_{29.9}$	0.601	2.3	42.7	3.5–6

[a] The initial molar ratio of Co/(Co + Ni) in preparation.
[b] The initial molar ratio of PVP (monomer)/(Co + Ni) in preparation.
[c] Reaction conditions: $T = 343$ K; $P = 4$ MPa; fructose/water/metal in catalyst = 21.43 g/50 g/2 mmol; reaction time = 1 h.

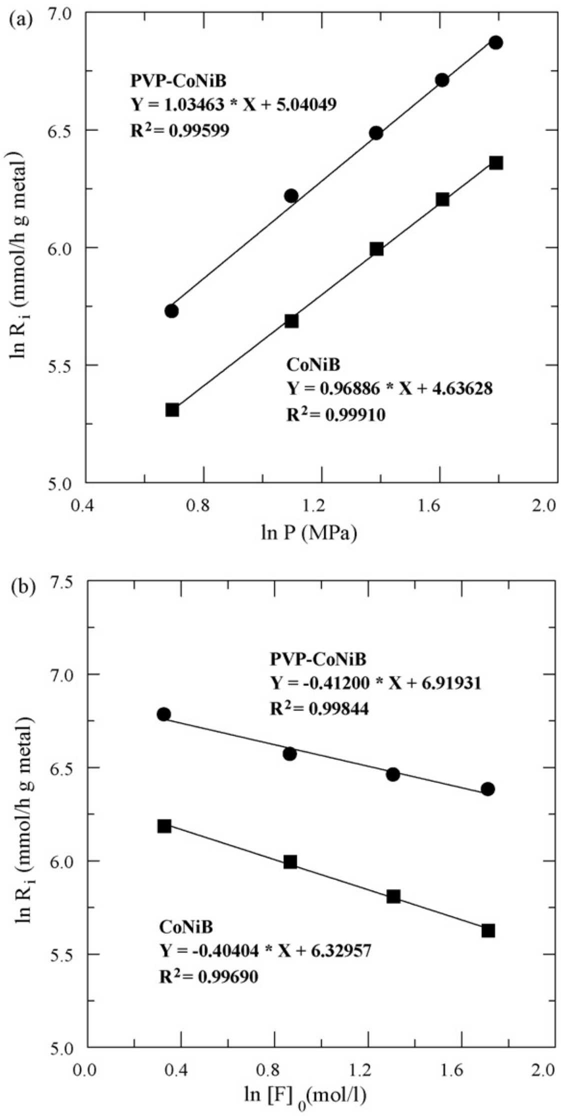

Fig. 4. Effects of pressure and fructose concentration on the hydrogenation of fructose.

28 kJ/mol for both CoNiB(0.6) and PVP(3)-CoNiB(0.6). This activation energy was lower than that (32.6 kJ/mol) over Raney nickel reported by Wisniak and Simon [30] for the hydrogenation of fructose at 5 MPa.

As presented in Fig. 4(a), the initial rates over CoNiB(0.6) and PVP(3)-CoNiB(0.6) at 343 K increased with the hydrogen pressure from 2 to 6 MPa, indicating that the fructose hydrogenation was first-order with respect to hydrogen pressure. In contrast, the initial rates at 343 K and 4 MPa decreased as the initial concentration of fructose ($[F]_0$) increased from 1.4 (20 wt.%) to 5.6 mol/l (50 wt.%) (Fig. 4(b)), indicating a negative-order dependence of −0.4 on fructose concentration. These orders for hydrogen and fructose reveal that the adsorption strength of fructose substantially exceeded that of hydrogen. As the reaction temperature exceeded 353 K, the competitive adsorption of hydrogen was much less favorable than that of fructose.

The hydrogenation of fructose over classical nickel-based catalysts gives selectivities of mannitol of between 45 and 50% [3,7]. The mannitol selectivity improved slightly over CoNiBs and PVP-CoNiBs. In aqueous solution, acyclic fructose is in equilibrium with its four cyclic forms. The mutarotation equilibrium of fructose solutions is temperature dependent. At 353 K, a fructose solution contains 53% β-fructopyranose, 2% α-fructopyranose, 32% β-fructofuranose, 10% α-fructofuranose and 3% open keto-form [3,7,31]. These different tautomeric forms of fructose have different adsorption strengths on hydrogenation catalysts. The hydrogenation of fructose over Cu and Ni catalysts has been claimed to proceed via the hydrogenation of the cyclic forms, and the furanose forms have been found to be more reactive than the pyranose forms [7,32]. Makkee et al. reported that β-fructose is converted to mannitol and α-fructose to sorbitol when fructose is hydrogenated over Cu/SiO_2 [32]. The inter-transformation between furanose species proceeds much faster than that between pyranose and furanose [33]. The inter-transformation between furanose species is not the rate-limiting step, because the mutarotation rate markedly exceeds the hydrogenation rate [7]. The selectivity of mannitol in fructose hydrogenation over CoNiB and PVP-CoNiB catalysts seems to depend on the fast mutarotation rate.

Table 2
Hydrogenation of invert sugar over CoNiB and PVP-CoNiB catalysts.

Catalyst	Conversion (%)[a]	Selectivity (%)[a]
NiB	6.8	45.4
CoB	n.d.	–
CoNiB(0.4)	11.5	42.5
CoNiB(0.5)	15.8	44.5
CoNiB(0.6)	10.8	44.0
PVP(2)-CoNiB(0.5)	22.4	42.5
PVP(3)-CoNiB(0.5)	30.9	41.3
PVP(5)-CoNiB(0.5)	31.3	39.7
Raney nickel	n.d.	–

[a] Reaction conditions: $T = 343$ K; $P = 4$ MPa; fructose/glucose/water/metal in catalyst = 10.71 g/10.71 g/50 g/2 mmol; reaction time = 1 h.

3.3. Hydrogenation of invert sugar

For economic reasons, mannitol is industrially prepared by the hydrogenation of invert sugar, which is a 1:1 mixture of glucose/fructose obtained by the hydrolysis of sucrose, generally using Raney nickel as a catalyst. The product typically obtained is a mixture of mannitol and sorbitol in the ratio 25/75 [1,7].

All of the as-prepared catalysts were used for the hydrogenation of invert sugar in aqueous solution at 343 K and 4 MPa. All CoNiB catalysts were more active than NiB, and much more active than CoB and Raney nickel (Table 2). The optimal molar fraction of cobalt in the CoNiB and PVP-CoNiB catalysts was shifted from the aforementioned 0.6 to 0.5, perhaps because of the different optimal adsorption states for pure fructose and invert sugar. The optimal catalyst of PVP(3)-CoNiB(0.5) was about twice as active as CoNiB(0.5). The mixture of glucose/fructose hydrogenated more slowly than fructose alone (Fig. 5), because glucose was adsorbed more strongly than fructose and thus inhibited the hydrogenation of fructose [1,7,30,32,34].

During the hydrogenation of invert sugar over CoNiB(0.5) and PVP(3)-CoNiB(0.5) catalysts at 343 K and 4 MPa, the selectivity of mannitol decreased as the reaction time increased, while maintaining a level above 30%. Maximum yields of mannitol of about 16% and 20% were obtained for CoNiB(0.5) and PVP(3)-CoNiB(0.5), respectively.

Although the selectivity of mannitol improved slightly in the hydrogenations of fructose and invert sugar over CoNiB and PVP-CoNiB catalysts, the activities significantly exceeded those of NiB and CoB, and even more exceeded that of Raney nickel to an even greater extent. The CoNiB and PVP-CoNiB catalysts are promising candidates for replacing Raney nickel in the hydrogenations of fructose and invert sugar.

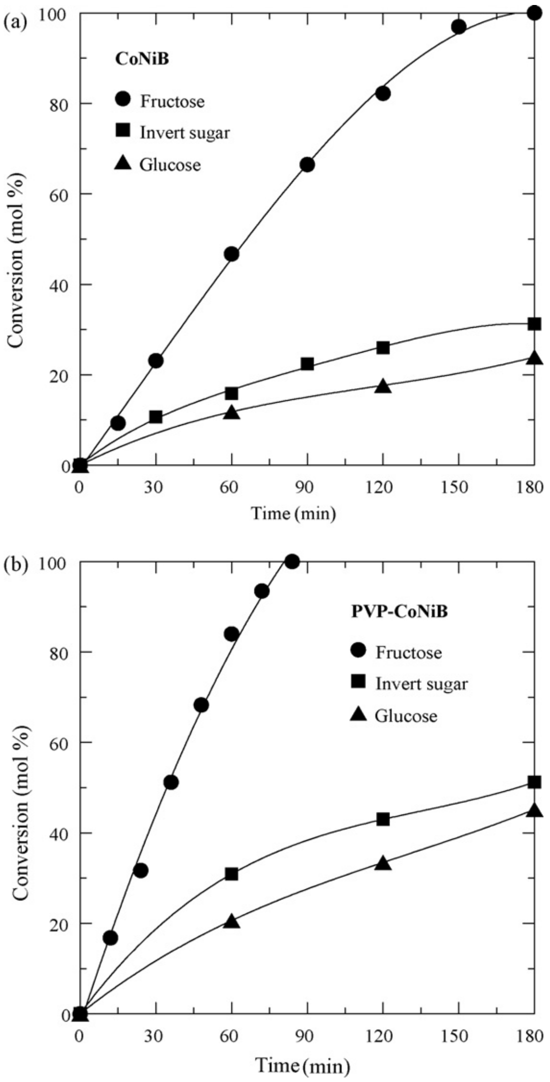

Fig. 5. Hydrogenation of fructose, invert sugar and glucose over CoNiB and PVP-CoNiB catalysts.

4. Conclusion

The bimetallic amorphous catalysts of CoNiB and PVP-stabilized CoNiB, prepared by chemical reduction, were characterized as 4–7 nm and 3.5–6 nm nano-sized particles, respectively. The optimal molar fraction of cobalt in CoNiB and PVP-CoNiB was about 0.6 for the hydrogenation of fructose, and about 0.5 for the hydrogenation of invert sugar. CoNiB and PVP-CoNiB were highly reactive in the hydrogenation of fructose and invert sugar. They were significantly more active than NiB and CoB, and much more active than Raney nickel. The initial rates of fructose hydrogenation exhibited a first-order dependence on hydrogen pressure (2–6 MPa) and a negative-order dependence of −0.4 on fructose concentration (1.4–5.6 mol/l). The competitive adsorption of sugar and hydrogen made the maximal rate occur at about 353 K. The selectivity of mannitol only changed slightly, perhaps because of the fast mutarotation equilibrium of fructose solutions.

Acknowledgements

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