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Applied Catalysis A: General 325 (2007) 34–40
APPLIED CATALYSIS A: GENERAL
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Selective maltose hydrogenation to maltitol on a ternary Co–P–B amorphous catalyst and the synergistic effects of alloying B and P

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Received 9 November 2006; received in revised form 31 January 2007; accepted 5 February 2007
Available online 13 February 2007

Abstract

A ternary Co–P–B amorphous alloy catalyst was prepared by chemical reduction with the mixed KBH_4 and NaH_2PO_2 in aqueous solution, and was characterized by ICP, XRD, SAED, TEM, SEM, XPS, H_2-TPD and hydrogen chemisorption. During liquid phase hydrogenation of maltose, the as-prepared Co–P–B catalysts exhibited 100% selectivity to maltitol and much higher activity than the Co–B, Co–P and Raney Ni, apparently owing to the synergistic promotions of the alloying B and P. More specifically, the alloying B increased the number of active sites (S_{act}) and donated partial electrons to the Co, which was favorable for the hydrogenation of the C=O group in the maltose. Furthermore, the alloying P led to the enhancement of the intrinsic activity (R_H^S) by forming new Co clusters as active sites. The maximum activity was obtained on the $Co_{72.2}P_{5.9}B_{21.9}$.

Keywords: Ternary Co–P–B amorphous alloy catalyst; Synergistic promotion; Hydrogenation; Maltose; Maltitol

1. Introduction

Hydrogenation of maltose to maltitol (Scheme 1) is of great industrial importance since maltitol is not only a sugar-free sweetener which could be used an additive for manufacturing foods for the diabetics, but even as an intermediate in production of pharmaceuticals [1–7]. Nickel-based catalysts are frequently used in the maltose hydrogenation [2–5], but the low selectivity to maltitol seems to be a problem. Ru-based catalysts display excellent activity and selectivity [6,7], but their industrial application is limited due to the high cost. Alloy catalysts with amorphous structure have been proven to possess very interesting catalytic properties in comparison with the corresponding crystalline counterparts and even Raney Ni, especially in hydrotreating reactions [8,9]. Our previous studies have proved that both the Co–B and Co–P amorphous alloys exhibited excellent catalytic properties in many hydrogenating reactions, including the hydrogenation of glucose to sobitol [10–13]. The Co–P displayed higher intrinsic activity and better selectivity than the Co–B. But the Co–B showed higher total activity, owing to the high dispersion degree of the active sites and the strong electronic interaction. Stimulated by these exciting results, we report here a ternary Co–P–B amorphous alloy catalyst with the aim to elucidate the synergistic effects between the alloy B and the alloying P on the catalytic properties during liquid phase hydrogenation of maltose to maltitol.

2. Experimental

2.1. Catalyst preparation

The Co–P–B samples were prepared by adding drop-wise 2.0 M KBH_4 aqueous solution into an aqueous solution containing 1.0 M $CoCl_2$ and 2.0 M NaH_2PO_2 at 303 K under vigorous stirring. The resulting black precipitate was washed free from Cl^-, K^+ or Na^+ ions with distilled water until the pH ~ 7, and finally soaked in water until the time of use. The molar ratio of (P + B)/Co was 6/1 to ensure the complete reduction of Co^{2+} ions. The P- and B-contents in the Co–P–B samples were adjusted by varying the molar ratio of P/B. For comparison, both the Co–P and the Co–B samples were also prepared according to the methods reported elsewhere [8,9]. Briefly, the Co–P was prepared by chemical reduction of 1.0 M $CoCl_2$ by 2.0 M NaH_2PO_2 in aqueous solution at 343 K under

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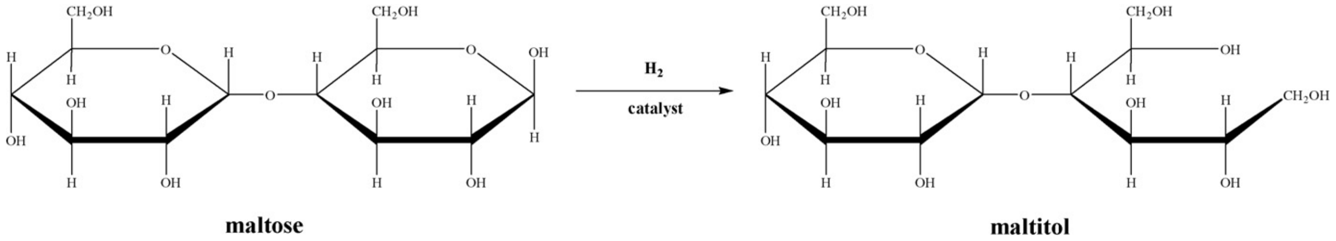
doi:10.1016/j.apcata.2007.02.007



Scheme 1. Catalytic hydrogenation of maltose to maltitol.

vigorous stirring, during which the pH value was controlled at 11.0 by using 2.0 M NaOH solution. Co–B amorphous alloy was prepared by a similar method to that for Co–P–B in the absence of NaH_2PO_2. Raney Ni was commercially available and was used without further treatment.

2.2. Catalyst characterization

The bulk composition was analyzed by means of inductively coupled plasma (ICP-AES, Jarrell-Ash Scan 2000). The amorphous structure and its alterations after heating pretreatments were investigated by X-ray diffraction (XRD, Rigaku Dmax-3C with Cu Kα radiation) and selected area electron diffraction (SAED, JEOL JEM-2011). The surface morphology and the particle size were observed by both scanning electron micrography (SEM, Philips XL-30) and transmission electron micrography (TEM, JEOL JEM-2011). X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer PHI 5000C ESCA system to determine the surface electronic states. The active surface area (S_{act}) was measured by hydrogen chemisorption on a Quantachrome CHEMBET 3000 assuming H/Co(s) = 1 and a surface area of 6.5×10^{-20} m^2 per Co atom [14]. The hydrogen TPD curves were obtained on the same instrument in argon flow at a ramp of 20 K/min.

2.3. Activity test

Liquid phase maltose hydrogenation was performed at 393 K in a 200 ml stainless steel autoclave containing 3.0 MPa H_2, 1.0 g Co and 50 ml 40% (w/w) maltose aqueous solution. Preliminary kinetic studies revealed that there was a plateau in the dependency of the reaction initial rate upon the stirring rate above 1000 rpm and that the reaction initial rate varied linearly with catalyst amount from 0.5 to 2.0 g, indicating that the stirring rate of 1200 rpm was high enough that the hydrogenation rates were independent of mass transfer. The initial rate of reaction was obtained by measuring the drop of P_{H_2} within the first 0.5 h, from which both the specific activity (the H_2 uptake rate per gram of Co, $R_H^m = \text{mmol}\,h^{-1}g_{Co}^{-1}$) and the areal activity (the H_2 uptake rate per square meter of Co, $R_H^S = \text{mmol}\,h^{-1}m_{Co}^{-2}$) were calculated by using the ideal gas equation. R_H^S could be considered as the intrinsic activity since the effect of metal dispersion has been excluded. After reaction for 4 h, the reaction products were analyzed in a liquid chromatograph (Agilent 1100) equipped with a carbohydrate column (CARBOSep, Coregel-87C) and a refractive index (RI) detector at 353 K with water as movable phase at 0.6 ml/min.

3. Results and discussion

The XRD patterns (Fig. 1) revealed that, besides a peak at around 20–30° corresponding to amorphous B and P oxides, all the Co–P, Co–B and Co–P–B displayed only one broad peak centered at $2\theta = 45^\circ$ indicative of the typical amorphous structure [15]. The Co–B catalyst exhibited the broader peaks than the Co–P, indicating the higher amorphous degree, which might be attributed to the stronger interaction between the metallic Co and the alloying B owing to the larger discrepancy of the atomic sizes between the Co and the B than that between the Co and the P [16–18]. That the structure-disordering-factor (δ_S) of Co–B was larger than that of Co–P was also confirmed by the extended X-ray absorption fine structure (EXAFS) analysis [19]. Meanwhile, the theoretical calculation based on the density functional theory (DFT) revealed that the bond length of the Co–B was 1.95 Å, less than that of the Co–P (2.24 Å) [20,21], which also confirmed that the interaction in Co–B was stronger than that in Co–P. The Co–P–B exhibited even higher amorphous degree than either the Co–B or the Co–P, which could be attributed to the disturbing effects on the structure from two metalloids. After the materials were treated at 873 K in N_2 for 2 h, various crystalline diffraction peaks corresponding to metallic Co and crystalline CoP alloy appeared, indicating the transformation from amorphous structure to the crystalline structure, together with partial decomposition of the Co–P–B alloy into metal Co and the Co–P alloy. From the SEM morphologies (Fig. 2), one could further

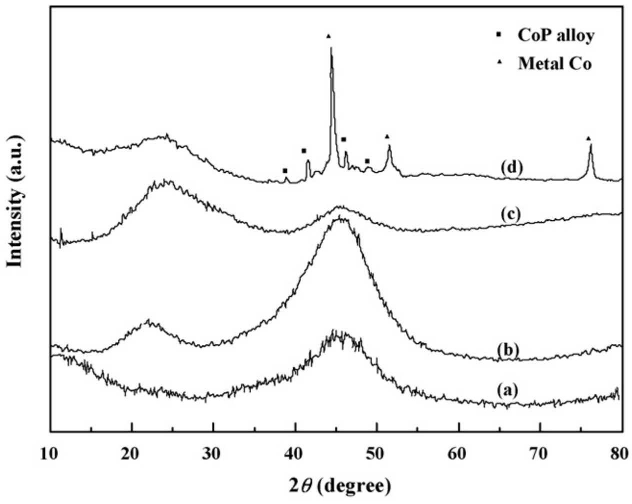


Fig. 1. XRD patterns of (a) the fresh Co–B, (b) the fresh Co–P, (c) the fresh Co–P–B, and (d) the Co–P–B treated at 873 K in N_2 flow for 2 h.