Applied Catalysis A: General 476 (2014) 34–38

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Chemoselective hydrogenation of aromatic aldehydes over SiO_2 modified Co/γ-Al_2O_3

Xiangjin Kong[a], Ligong Chen[b,c,*]

[a] Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China
[c] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, PR China

ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form 21 January 2014
Accepted 8 February 2014
Available online 18 February 2014

Keywords:
Chemoselective hydrogenation
Aromatic aldehyde
Benzyl alcohol
Hydrogenolysis
Co/γ-Al_2O_3–SiO_2

ABSTRACT

With benzaldehyde as a model compound, the hydrogenation of aromatic aldehydes to corresponding benzyl alcohols was investigated in a fixed-bed reactor. Co/γ-Al_2O_3 doped with a amount of SiO_2 displayed excellent catalytic performance for this reaction, Co/γ-Al_2O_3 is modified by SiO_2 in two ways, the strong interaction between metal oxide and support is obviously reduced, and also a large number of acid sites are diminished on the catalyst. The first aspect apparently facilitated the reduction of metal oxide, and improved the hydrogenation activity of the catalyst; while the second aspect greatly inhibited the hydrogenolysis of the —C—O bond, and thus increased the selectivity toward benzyl alcohol.

1. Introduction

Benzyl alcohols are a key class of intermediates in organic chemistry [1–3]. For example, benzyl alcohol is a commercially important chemical, employed as solvent for inks, paints, lacquers and as precursor for the manufacture of a range of esters in the cosmetics and flavoring industries [4]. However, the traditional production methods for these alcohols are always present a serious impact on the environment [5,6]. As an alternative route, chemoselective hydrogenation of aromatic aldehydes to obtain benzyl alcohol has drawn people's more attention. Several noble metals (Pd, Pt, Rh and Ru) have been reported for this reaction [7–11]. Unfortunately, the hydrogenation selectivity of C=O is still a challenge, since catalytic hydrogenolysis of benzyl alcohols to corresponding methyl arenes easily occur [11,12]. Nowadays, transition metals (Cu, Co and Ni) are frequently employed for hydrogenation reaction instead of the expensive noble catalyst [13–15]. Whereas, there are only a few reports concerned about the chemoselective hydrogenation of aromatic aldehydes over transition metals catalysts, and which often suffered from poor benzyl alcohols yield [16–18]. In our previous studies, a series of Ni and Cu based catalysts have been developed and exhibited excellent performance for the hydrogenation of carbonyl compounds [15,19–21]. These results encouraged us to study the chemoselective hydrogenation of aromatic aldehydes over transition metals catalysts.

In this work, benzaldehyde is used as a model molecule to evaluate catalyst for reduction of aromatic aldehydes to corresponding benzyl alcohols. Several Co based catalysts were examined, and in which SiO_2 modified Co/γ-Al_2O_3 exhibited excellent performance. The effects of SiO_2 doped in Co/γ-Al_2O_3 were studied by X-ray diffraction (XRD), H_2-temperature programmed reduction (H_2-TPR), NH_3-temperature programmed desorption (NH_3-TPD) and nitrogen adsorption/desorption measurement. Additionally, the selected catalyst is applied in the reduction of a collection of representative aromatic aldehydes.

2. Experimental

2.1. Materials and catalysts

Aromatic aldehydes were purchased from Tianjin Guangfu Finechemical institute. Pseudo-boehmite was supplied by Jiangyan Chemical Auxiliary Factory (Jiangyan, China). All the commercially available solvents and reagents were used without further purification.

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* Corresponding author. Tel.: +86 22 27406314; fax: +86 22 27406314.
E-mail address: lgchen@tju.edu.cn (L. Chen).

http://dx.doi.org/10.1016/j.apcata.2014.02.011
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Table 1
The reaction results of benzaldehyde over Co based catalysts.

Catalyst	Conversion (%)	Selectivity (%)			
		Methylcyclohexane	Toluene	Benzyl alcohol	Other
$Co_{20}/\gamma\text{-}Al_2O_3$	85.5	0.0	57.6	41.9	0.5
$Co/\gamma\text{-}Al_2O_3\text{–}48\%SiO_2$	90.6	0.0	25.6	73.8	0.6
$Co/\gamma\text{-}Al_2O_3\text{–}64\%SiO_2$	98.0	0.0	4.6	95.0	0.4
$Co/\gamma\text{-}Al_2O_3\text{–}72\%SiO_2$	95.8	0.0	8.5	91.1	0.4
Co/SiO_2	90.5	0.9	10.6	88.0	0.5

In the present studies, the cobalt weight percent on the catalyst is 20%. $Co/\gamma\text{-}Al_2O_3$ was prepared by kneading a mixture of pseudo-boehmite together with the corresponding precipitates of metal carbonates or hydroxides [15]. $Co/\gamma\text{-}Al_2O_3\text{–}m SiO_2$ (m means the weight percent of SiO_2 in the catalyst) was prepared by kneading a mixture of SiO_2 and pseudo-boehmite together with the precipitates of cobalt carbonates or hydroxides. For example, $Co_{20}/\gamma\text{-}Al_2O_3\text{–}64\%SiO_2$ (namely, the weight percent of SiO_2 in the support is 80%) was prepared as follows: 20.2 g metal carbonates were kneaded with a mixture of 32.0 g SiO_2 and 12.1 g pseudo-boehmite, followed by molding to bars (with a diameter of 3 mm) by an extruder. After drying in air at 110 °C for 6 h, the catalysts were calcined at 500 °C for 4 h. The Co based catalysts were reduced at 400 °C for 4 h in a stream of hydrogen under 1.0 MPa before use.

2.2. Catalysts characterization

Powder X-ray diffraction (XRD) was performed on a Rigaka D/max 2500 X-ray diffractometer, using Cu Kα radiation and scanning 2θ from 15° to 85°, operated at 40 kV and 100 mA. H_2-temperature programmed reduction (H_2-TPR) was measured using a micromeritics 2910 apparatus with a temperature ramp from 130 °C to 850 °C at 10 °C/min, and a gas flow of 5% H_2 in argon (20 mL/min). A thermal conductivity detector (TCD) was used to determine the amount of hydrogen consumed during temperature ramping. NH_3-temperature programmed desorption (NH_3-TPD) was carried out on a TP-5000 instrument with a thermal conductivity detector (TCD). The BET (Brunauer–Emmett–Teller) specific surface areas, pore-size distributions, total pore volumes and sorption isotherms of the materials were measured via nitrogen adsorption/desorption using a NOVA 2000e analyzer (Quantachrome, US).

2.3. Catalytic test

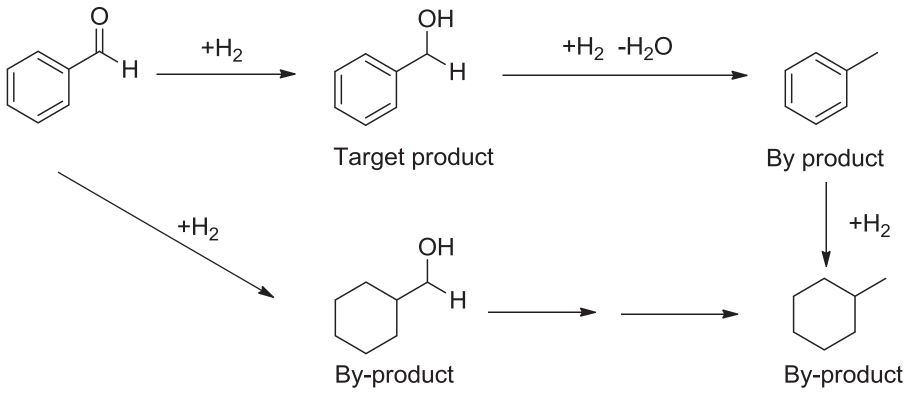
Activity measurement was performed in a fixed bed reactor, which was loaded with about 18.0 g catalysts (cylinder catalyst particle with diameter of 3 mm and height about 2–3 mm), under an atmosphere of 3 MPa H_2 and a reaction temperature of 130 °C. A solution of aromatic aldehydes (concentration in 1,4-dioxane = 20.0 wt%) was dosed into the reactor at a flow rate of 0.2 mL/min by a pump. The components of the reaction mixture was confirmed by GC–MS (Polaris Q, Thermo Finngan, America, HP-1 capillary column, 30 m × 0.25 mm, 0.2 μm film thickness) equipped with an ion trap MS detector. The composition of the reaction mixture was monitored by GC with an OV-1701 capillary column (30 m × 0.25 mm, 0.2 μm film thickness).

3. Results and discussion

3.1. Catalyst modification

Co based catalysts were frequently employed in the hydrogenation reaction, and $\gamma\text{-}Al_2O_3$ was a widely used support for metallic catalyst [20–23]. Therefore, $Co/\gamma\text{-}Al_2O_3$ was prepared and employed for the reduction of benzaldehyde firstly; the obtained results are listed in Table 1. Besides the desired product benzyl alcohol, a considerable amount of toluene was also detected. Barbelli et al. [24] and Wu et al. [25] had reported that strong acidic sites on catalysts are helpful for the hydrogenolysis of —C—O bond. Considering of this, we inferred that the toluene was possibly generated from the hydrogenolysis of benzyl alcohol. According to the above results, the reaction pathway was deduced and shown in Scheme 1. As well known, SiO_2 has lower acidity than $\gamma\text{-}Al_2O_3$. Thus, it was added to $Co/\gamma\text{-}Al_2O_3$ to decrease its acidity, and the results over these modified catalysts are shown in Table 1.

As described in Table 1, with the addition of 64 wt% SiO_2 to the catalyst, the selectivity of benzyl alcohol increased from 41.9% to 95.0%, while the conversion of benzaldehyde increased from 85.5% to 98.0%. Table 1 also displayed that when the percent of SiO_2 in the catalyst is more than 64 wt%, both the selectivity of benzyl alcohol and conversion of benzaldehyde were slightly decreased. These results demonstrated that the catalytic properties of the catalyst in hydrogenation and hydrogenolysis were evidently influenced by the introduction of SiO_2, and $Co_{20}/\gamma\text{-}Al_2O_3$ doped with 64 wt% SiO_2 displayed an excellent catalytic performance for the present reaction. To better understand the effects of doped SiO_2, $Co/\gamma\text{-}Al_2O_3$,



Scheme 1. The reaction pathway for chemoselective hydrogenation of benzaldehyde.