CHEMICAL KINETICS AND CATALYSIS

Liquid-Phase Hydrogenation of Benzaldehyde on Low-Percentage Pt-Containing Catalysts under Mild Conditions

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Abstract—The reaction of the liquid-phase hydrogenation of benzaldehyde is studied in two modes: at room temperature and atmospheric pressure, and at a temperature of 70°C and a pressure of 0.5 MPa on Pt/CeO₂–ZrO₂ catalysts with metal contents of 1 to 0.025 wt %. A 96% conversion of benzaldehyde is obtained on 1% Pt/CeO₂–ZrO₂ catalysts at room temperature, while a 97% conversion is obtained on 0.1% Pt/CeO₂–ZrO₂ catalysts at elevated temperatures. The selectivity of the formation of benzyl alcohol is in all cases 100%.

Keywords: benzaldehyde, benzyl alcohol, selective hydrogenation, mild conditions, platinum-containing catalyst

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INTRODUCTION

Benzyl alcohol (BnOH) is an important intermediate in the production of paints, varnishes [1], and vitamins [2]. It is also widely used in the chemical industry as a precursor for the synthesis of various esters and fragrances [3].

In industry, there are two main ways of producing benzyl alcohol: the hydrolysis of benzyl chloride with sodium hydroxide, and the oxidation of toluene. In the first case, the process proceeds at high temperatures (150–350°C) and elevated pressures. The formation of ether as a by-product is possible during the reaction. This process is also complicated by the formation of large amounts of chlorine-containing waste requiring disposal [4]. Toluene is oxidized in the presence of acetic anhydride at temperatures of 170–220°C and pressures of 1–3 MPa [5]. The main disadvantage of this technique is the formation of benzaldehyde and benzoic acid upon further oxidation, which greatly reduces the yield of alcohol.

The production of benzyl alcohol via the catalytic hydrogenation of benzaldehyde on heterogeneous catalysts allows to conduct an industrially important process in accordance with the principles of green chemistry. An industrial catalytic process for the selective hydrogenation of benzaldehyde is the reduction of the carbonyl group using Raney Ni at temperatures of 80–120°C [6]. Under such conditions, however, large amounts of such by-products as toluene, hydroxymethylcyclohexane (HydroxyMCH), and benzene can form, reducing the efficiency of the process.

The use of noble metal catalysts can greatly reduce the reaction temperature and hydrogen pressure. The development of catalysts that have low contents of noble metals and are active and selective under mild conditions could be an alternative, more economical and efficient way of obtaining BnOH. Carrying out the reaction of benzaldehyde hydrogenation on a commercial catalyst 1% Pd/C allowed to obtain BnOH with a selectivity of 99% at room temperature and a pressure of 0.8 MPa. However, the conversion after 1 h of the reaction was only 11%, and complete conversion under these conditions was achieved in 24 h [7]. BnOH was obtained with a selectivity of 99% on a 5% Pt/TiO₂ catalyst at a substrate conversion of 85%, at room temperature and a pressure of 4 MPa [8]. However, both the performance of the catalysts and the conditions of the reaction can be improved markedly.

In this work, the reaction of liquid-phase benzaldehyde hydrogenation (Fig. 1) was carried out on heterogeneous catalysts with Pt contents of ≤1 wt %, supported on CeO₂–ZrO₂ mixed oxide at room temperature and atmospheric pressure, and at a temperature of 70°C and a hydrogen pressure of 0.5 MPa.

EXPERIMENTAL

Preparation of Catalysts

Mixed oxide carriers CeO₂–ZrO₂ (CZ) were synthesized via the coprecipitation of metal precursors [9] ZrO(NO₃)₂·8H₂O (99.5%; up to 4% Hf; Acros) and (NH₄)₂Ce(NO₃)₆ (98+%, Alfa Aesar).

Fig. 1. Benzaldehyde hydrogenation reaction.

Catalysts with platinum contents of 1–0.025 wt % were synthesized via the pH-controlled precipitation from H_2PtCl_6 as precursor. The resulting samples were reduced for 2 h in a stream of hydrogen at a temperature of 250°C.

Catalysts Characterization

The catalysts were investigated by means of temperature-programmed reduction with hydrogen (TPR- H_2) in a laboratory flow system with a water trap cooled to -100°C . The sensitivity of the thermal conductivity detector was calibrated by the reduction of CuO as the standard (Aldrich-Chemie, 99%) preliminarily treated for 90 min in Ar (30 mL/min at 300°C). Pt/CZ catalysts (140–170 mg) were pretreated in an Ar flow with an oxygen trap at 250°C . Before each TPR experiment, the sample was cooled to room temperature (25°C) or to -100°C in an Ar flow. The samples were heated from -100 to 250°C at a rate of 10 K/min in a gas mixture of 4.6% H_2 -Ar (also purified with an oxygen trap) at a flow rate of 30 mL/min. The samples were kept at the required temperature (25 or 250°C) until the absorption of hydrogen ceased.

The phase composition of the materials and the sizes of particles were investigated via X-ray diffraction (XRD). XRD patterns were recorded using an ARL X'TRA diffractometer (Thermo Fisher Scientific) with $\text{CuK}\alpha$ radiation (40 kV, 40 mA) at a scanning rate of 1.2 deg/min in the range of $20^\circ < 2\theta < 70^\circ$.

Hydrogenation of Benzaldehyde

Experiments on liquid-phase hydrogenation at room temperature and atmospheric pressure were per-

formed using a two-necked glass flask as a reactor. The catalyst (50 mg) was placed in a reactor, and the system was sealed and purged with hydrogen for 30 min. A solution of benzaldehyde in EtOH (0.3 mmol of the substrate in 1.5 mL of the solvent) was then poured into the reactor using a 3-way valve for feeding the reaction mixture. The amount of Pt in the reaction mixture was 0.4–0.8 mol %, depending on the content of metal in the catalyst. The reaction mixture was stirred for 2 h with a magnetic stirrer at 1400 rpm.

Experiments at 70°C and a hydrogen pressure of 0.5 MPa were performed in a stainless steel autoclave with a glass insert. A solution of benzaldehyde in EtOH (0.3 mmol of substrate in 1.5 mL of solvent) and the required amount of catalyst (50 mg) were introduced into the reactor. Before the start of each experiment, the reactor was purged with hydrogen 3 times to remove residual air. The reaction volume was then filled with hydrogen at a pressure of 0.5 MPa. The reaction was conducted for 2 h at a stirring speed of 1400 rpm. At the end of each experiment, the liquid phase was separated from the catalyst via centrifugation to analyze the composition of the reaction products.

Liquid reaction products were analyzed on a Chromatech Crystal 5000.2 gas chromatograph equipped with a flame ionization detector and a CR-5 capillary column (0.2 mm $\times$ 25 m). The column temperature was raised stepwise from 80 to 190°C . Peaks were identified using experimentally determined retention times of individual compounds (benzaldehyde, benzyl alcohol, ethanol). The structure of the obtained compounds was confirmed using NMR ^1H and ^{13}C spectroscopy.

Table 1. Morphological and textural properties of the CZ carrier

Ce : Zr ratio	Phase composition (according to XRD)	Average nanoparticle size, nm (XRD)	S_{BET} , m^2/g	Pore volume, cm^3/g	Pore size, nm
4 : 1	CeO_2 cubic phase ZrO_2 amorphous phase	4	103	0.145	2–10

Table 2. Results from our TPR-H₂ study of preliminarily reduced catalysts

Sample I	H ₂ absorption, mmol/g	H ₂ /Pt, mol/mol	Sample II	H ₂ absorption, mmol/g	H ₂ /Pt, mol/mol
CZ	0	—	CZ	0	—
1%Pt/CZ	0.67	13	0.1%Pt/CZ	0.55	86
0.5%Pt/CZ	0.45	18	0.05%Pt/CZ	0.72	228
0.25%Pt/CZ	0.11	8	0.025%Pt/CZ	0.47	348

The absorption of hydrogen for samples I was measured in the -50 to 25°C range of temperature. It was measured in the -50 to 250°C range for samples II.

RESULTS AND DISCUSSION

The key characteristics of the mixed ceria–zirconia support are given in Table 1. They were also described in detail in our previous works [10, 11].

TPR-H₂ studies of the catalysts and catalytic experiments were performed in two modes, in order to study the properties of the samples under conditions close to those of the reaction. The study of preliminary reduced catalysts with platinum contents of 1–0.25% showed that samples of 1% Pt/CZ and 0.5% Pt/CZ had the greatest absorption of hydrogen in the -50 to 25°C range of temperatures (0.67 and 0.45 mmol/g, respectively) (Table 2). The hydrogen uptake by the 0.25% Pt/CZ catalyst in this temperature range was substantially lower than those of 1% Pt/CZ and 0.5% Pt/CZ, and totalled 0.11 mmol/g. Even at such low contents of the noble metal, however, we observed the absorption of H₂ at room temperature. It should be noted that the hydrogen/metal molar ratio in all three cases greatly exceeded the stoichiometric ratio, which could indicate the presence of H₂ spillover in the given range of temperatures, which was characterized by an overflow of “active” hydrogen formed on the centers of metallic platinum onto the reducible CeO₂–ZrO₂ support.

TPR-H₂ study of the catalysts with platinum contents of 0.1% or less was performed in the -50 to 250°C range of temperatures. The hydrogen uptake by the catalyst with a platinum content of 0.1% was 0.55 mmol/g. There was a slight increase in the H₂ uptake in this temperature range on the sample with a platinum content of 0.05%. This effect could be associated with additional reduction of the deposited active phase during TPR analysis, since all samples were preliminarily treated at the same temperature (250°C). However, it is known that an increase in the interaction between the metal phase and the support can be observed upon reducing the amount of deposited metal (and thus the size of particles or clusters), so a higher temperature could be needed for complete reduction than in case of larger particles [12]. It should also be noted that the reduction of cerium oxide in the carrier without supported metal started at temperatures above 250°C .

As noted earlier, the main difficulty in the hydrogenation of benzaldehyde is the selective reduction of the carbonyl group without the hydrogenation of the aromatic ring or hydrogenolysis. It was assumed that conducting the reaction under mild conditions would help avoid the formation of such products as HydroxyMCH and toluene (Fig. 1).

Our studies of catalysts with platinum contents of 0.25–1% (Fig. 2a) that were performed at room temperature and atmospheric pressure showed that halv-

Fig. 2. Hydrogenation of benzaldehyde (a) on catalysts with a Pt 1 content of 0.1 wt % at room temperature and atmospheric pressure; (b) on catalysts with Pt contents of 0.1–0.025 wt % at a temperature of 70°C and a H₂ pressure of 0.5 MPa.

ing the content of Pt (from 1 to 0.5%) affects the conversion of benzaldehyde (96 and 93%, respectively) negligibly. This is consistent with results from studying the absorption of hydrogen, where the volume of H_2 absorbed by 1% Pt/CZ and 0.5% Pt/CZ samples differed by only a factor of 1.5. Drops in the conversion of the substrate (43 and 14% when using 0.25% Pt/CZ and 0.1% Pt/CZ catalysts, respectively) were noted upon subsequent reductions in the content of the noble metal.

Even though samples with low contents of platinum were less active at room temperature and atmospheric pressure, we may assume they have high activity when tested at elevated pressures and/or temperatures, due to the observed intense absorption of hydrogen up to 250°C. Catalysts with Pt contents of ≤ 0.1 wt % were tested at 70°C and a pressure of 0.5 MPa (Fig. 2b). The yield of BnOH on the 0.1% Pt/CZ sample was 97%, and it remained high when using a catalyst with a platinum content of 0.05%. Even the 0.025% Pt/CZ catalyst was also active under these conditions, and the yield of BnOH was 70%.

Mironenko et al. investigated monometallic Pd- and Ru-containing catalysts under similar conditions (a temperature of 40°C and a pressure of 0.5 MPa) in the liquid-phase hydrogenation of benzaldehyde [1]. Complete conversion of the substrate was achieved after 1 h on a catalyst with a palladium content of 1.5%. However, the selectivity of BnOH formation was only 42%, due to the predominant formation of toluene. The selectivity of BnOH formation on a Ru-containing sample (1.5 wt %) was 44%, but the conversion of benzaldehyde was half that of the sample with supported palladium.

Mironenko's group also investigated low-percent-age palladium-containing catalysts [13]. The conversion of benzaldehyde was 48% when using a sample with a metal content of 0.3% at a temperature of 60°C and a pressure of 0.5 MPa. BnOH was in this case the only reaction product.

It should be noted that at room temperature and atmospheric pressure, and at a temperature of 70°C and a pressure of 0.5 MPa, catalysts supported on mixed ceria–zirconia supports were much more active than samples based on CeO_2 alone, which were described by our group earlier. Adding zirconium oxide both enhances the spillover of hydrogen and helps to create additional defects, which may act as additional centers for the selective adsorption of carbonyl groups.

CONCLUSIONS

It was shown that platinum-containing catalysts based on a mixed ceria–zirconia support allow us to obtain benzyl alcohol by hydrogenation of benzaldehyde with 100% selectivity. Samples with Pt contents

of 1–0.5 wt % exhibited high activity at room temperature and atmospheric pressure, while catalysts containing ultra-low amounts of Pt (0.025 to 0.1 wt %) displayed high activity in the hydrogenation of benzaldehyde at a temperature of 70°C and a pressure of 0.5 MPa.

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