Applied Catalysis A: General 500 (2015) 23–29

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Tuning catalytic selectivity of liquid-phase hydrogenation of furfural *via* synergistic effects of supported bimetallic catalysts

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ARTICLE INFO

Article history:
Received 7 January 2015
Received in revised form 28 March 2015
Accepted 9 May 2015
Available online 16 May 2015

Keywords:
Bimetallic catalysts
Synergistic effect
Hydrogenation
Furfural
Catalytic selectivity

ABSTRACT

Bimetallic catalysts supported over TiO_2–ZrO_2 binary oxides were prepared by co-impregnation methods and used for catalyzing liquid-phase hydrogenation of furfural. Highly selective hydrogenation catalysts can be developed based on bimetallic synergistic effect. The coexistence of small proportion of palladium with supported nickel species greatly improves the catalytic performance and transfer the reaction selectivity from partial hydrogenation to total hydrogenation. The catalyst with Ni–Pd mole ratio of 5:1 shows the best performance. The yield of tetrahydrofurfuryl alcohol (THFA) reaches 93.4%. Ni–Pd synergistic effect is interpreted through XPS measurement and a hydrogen-transfer mechanism is proposed. Pt–Re bimetallic catalyst is an excellent partial hydrogenation catalyst for furfural conversion. Furfural can be totally converted and the selectivity of partial hydrogenation product (FA) reaches 95.7%. When rhenium oxide species are located on the Pt surface, the hydrogen species on Pt are transferred to adsorbed C=O bond to achieve selective hydrogenation.

1. Introduction

Limited fossil fuel resources and global warming issues stimulate great research efforts in sustainable production of fuel and chemicals from renewable biomass in recent decades. Furfural from acidic hydrolysis of hemicellulose is the most promising biomass platform chemical that can be manufactured through large-scale industrial process [1]. Through catalytic hydrogenation, furfural can be converted to furfuryl alcohol (FA) and tetrahydrofurfuryl alcohol (THFA). Furfuryl alcohol is widely used to manufacture foundry resins, synthetic fiber, farm chemicals, adhesives and fine chemicals such as vitamin and lysine [2–5]. THFA is considered as a green solvent and used in agricultural applications, printing inks, and industrial and electronics cleaners [6]. Furfural molecule has several active functional groups. There are many possible conversion routes during catalytic hydrogenation, including partial hydrogenation to FA, total hydrogenation to THFA and various possible side reactions such as heat-driven oligomerization, hydrogenolysis of side-substituents to 2-methylfuran, decarbonylation to furan and rearrangement to levulinic acid, and furan ring opening [7]. The core issue of furfural hydrogenation is how to control its reaction route and hydrogenation degree through using highly selective catalyst.

The performance of heterogeneous hydrogenation catalysts is directly related to active metals and supports [8]. Supported noble and non-noble metals have been reported for hydrogenation of FR. Conventional production of THFA is based on a two-step strategy: hydrogenation of furfural FA over Cu–Cr catalyst and further hydrogenation of FA to THFA over supported noble catalysts. Direct hydrogenation of furfural to THFA has been achieved over Ni–Pd/SiO_2 [9], Ni/SiO_2 [10] and Pd/MFI [11] catalysts. The catalysts for hydrogenation of furfural to FA are supported Ni, Co, Cu, Ru, Pd and their bimetallic catalysts [2,12,13]. Pt-based catalysts are rarely used for producing FA from furfural due to complex side reactions (hydrogenolysis of the C—O bond, decarbonylation, total hydrogenation and furan ring opening, *etc.*) [14]. It has not been reported that the hydrogenation degree can be adjusted through synergistic effects of bimetallic catalytic system. It is of great significant to achieve both selective hydrogenation and total hydrogenation of furfural through a well-define bimetallic mechanism.

Physicochemical properties of the catalyst's support markedly influence its performance for liquid-phase catalytic hydrogenation of unsaturated aldehydes and ketones [8]. TiO_2–ZrO_2 mixed oxides exhibit high surface area, profound surface acid-base properties, a high thermal stability, and strong mechanical strength [15]. TiO_2–ZrO_2 mixed oxides are used as catalysts and catalysts supports for various reactions [16]. TiO_2–ZrO_2 supported Pt species are

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http://dx.doi.org/10.1016/j.apcata.2015.05.006

the most selected catalysts for hydrogenation conversion such as naphthalene hydrogenation [17], selective hydrogenation of furfural [12], and selective hydrogenation of crotonaldehyde [18]. TiO_2–ZrO_2 mixed oxides are used as supports of bimetallic catalysts for selective furfural hydrogenation.

In this work, Ni–Pd over TiO_2–ZrO_2 was selected as model catalytic system to investigated synergistic effects of bimetallic catalysts upon selectivity of liquid-phase furfural hydrogenation. Raney Ni and Pd/C were used as benchmarked catalysts. The bimetallic catalysts with various ratio of Ni to Pd were screened and the experimental results showed marked synergistic effects. The corresponding mechanism was revealed by XPS measurement. In further investigation, the selectivity of Pt-M/TiO_2–ZrO_2 bimetal catalysts (M = Re, Sn, In) for furfural hydrogenation was explored and a different trend of bimetallic synergistic effect was observed.

2. Experiment

2.1. Materials and chemicals

Titanium butoxide, Zirconium (IV) butoxide solution (80 wt% in n-butanol), dodecyl amine (DDA), nickel nitrate hexahydrate, furural, ethanol, toluene, dioxane, and 2-propanol were purchased from Sinopharm Chemical Reagent. H_2PtCl_6, $KReO_4$, $PdCl_2$, Pd/C and Raney Ni were purchased from Strem. $SnCl_4·5H_2O$ and $In(SO_3CF_3)_3$ were obtained from Alfa Aesar. All the reagents were used as received except furfural, which was used after vacuum distillation.

2.2. Catalyst preparation

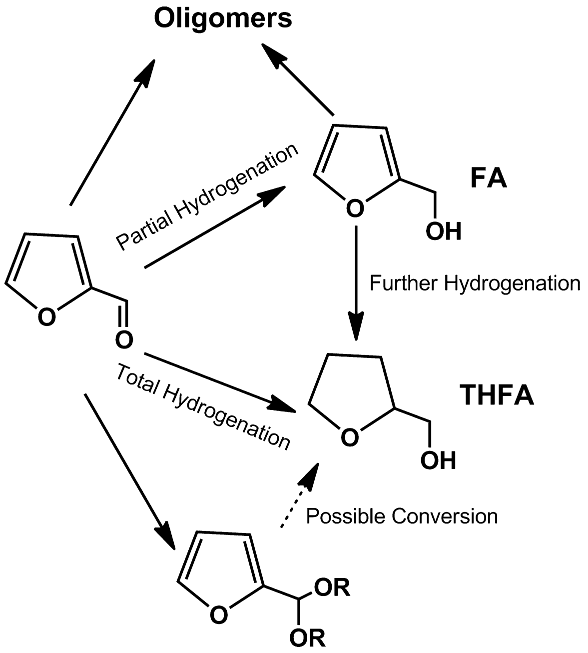
TiO_2–ZrO_2 mixed oxide support (1:1, mole ratio) was prepared by the sol–gel method reported by our group [19]. All catalysts were prepared by co-impregnation or impregnation of metal precursors onto TiO_2–ZrO_2 binary oxide support. The calculated amount of TiO_2–ZrO_2 was impregnated with a certain concentration aqueous solution of metal precursors (such as $PdCl_2(CH_3CN)_2$, $Ni(NO_3)_2·6H_2O$, H_2PtCl_6, $KReO_4$ $SnCl_4·5H_2O$ and $In(SO_3CF_3)_3$) and kept in an oven at 383 K overnight. Then these solids were calcined at 723 K in air for 3 h. These catalysts were activated under flowing diluted hydrogen (H_2/Ar: 10%) at 673 K for 3 h before testing.

2.3. Catalytic activity measurements

Catalytic hydrogenation of furfural was performed in a 100 ml stainless autoclave equipped with a pressure gauge, a magnetic stirrer, and an electric temperature controller. The catalyst (200.0 mg), the solvent (8.5 ml) and furfural (1.5 ml) were introduced into the reactor. The sealed autoclave was flushed with H_2 three times, pressurized with H_2 to 5.0 MPa, and started to stir. After the designated temperature was reached, the reaction began. At the end of reaction, the autoclave was cooled to ambient temperature and slowly depressurized. The conversion and product composition were analyzed by GC and GC–MS. GC was performed on a GC-2014 (SHIMADZU) equipped with a high-temperature capillary column (MXT-1, 30 m, 0.25 mm ID) and a FID detector. GC–MS was performed on a GCT Premier/Waters instrument equipped with a capillary column (DB-5MS/J&W Scientific, 30 m, 0.25 mm ID).

2.4. Catalyst characterization

Powder X-ray diffraction (XRD) patterns was measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode and a Cu-Kα radiation source (40 kV, 200 MA; $\lambda = 1.54056$ Å). XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-Kα radiations. The base pressure was approximately 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The Eclipse V2.1 data analysis software supplied by the VG ESCA-Lab200I-XL instrument manufacturer was used to manipulate the acquired spectra. Transmission electron microscopy (TEM) was performed on a JEOL 2010 TEM equipped with an attachment for local energy dispersion analysis (EDX). The accelerating voltage was 200 kV, and the spot size was 1.0 nm.



Scheme 1. Illustration of reaction routes of furfural hydrogenation.

3. Results and discussions

3.1. Hydrogenation of furfural over Ni–Pd bimetallic catalysts

Scheme 1 shows reaction route map of liquid-phase hydrogenation of furfural in alcohol solvents. There are two target molecules: partial hydrogenation product (FA) and total hydrogenation product (THFA). Cu–Cr mixed oxides are the classic catalysts for partial hydrogenation of furfural. However, leached toxic Cr species pose serious environmental issues. Nickel-based catalysts are considered as potential replacement. The main drawback of nickel hydrogenation catalyst is that active zero-valent nickel species are highly sensitive to oxygen. It is difficult to keep nickel catalysts in their primary activated states. Fresh commercial Raney Ni shows low catalytic activity and poor selectivity of FA (Entry 1 in Table 1). Nickel over TiO_2–ZrO_2 binary oxide has improved catalytic activity for partial hydrogenation of furfural and the yield of FA reaches 69.2% (Entry 2 in Table 1). The reaction over the supported Pd catalyst mainly produces total hydrogenation product. The yield of THFA is 62.2% for furfural hydrogenation over commercial Pd/C and the value increases to 78.6% for palladium over TiO_2–ZrO_2 binary oxide (Entry 3, 4 in Table 1).

When nickel and palladium precursors are introduced onto TiO_2–ZrO_2 through co-impregnation, Ni–Pd/TiO_2–ZrO_2 bimetallic catalyst is obtained. The coexistence of nickel and palladium lead to marked synergistic effects and enhance the catalytic performance significantly (Entry 5–8 in Table 1). Ni–Pd bimetallic catalysts show higher hydrogenation activity than anyone of the two mono-metallic catalysts. The yield values of hydrogenation products are above 90% and the percentage of byproducts is very low. Though adjusting the mole ratio of nickel to palladium, the catalytic selectivity is finely tuned to only one type of hydrogenation