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Article

Surface titanium oxide loaded on a special alumina as high-performance catalyst for reduction of cinnamaldehyde by isopropanol

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ABSTRACT

A nanocomposite catalyst with a nonstoichiometric titanium oxide loaded on a special nanotubular alumina (γ-Al_2O_3-nt) was developed and used to reduce cinnamaldehyde to cinnamyl alcohol with sacrificial isopropanol, i.e., a Meerwein-Ponndorf-Verley type reaction. The deposition process produced a highly disperse layer of titanium oxide on the surface of a γ-Al_2O_3-nt support. After a reduction treatment, the as-prepared TiO_x/γ-Al_2O_3-nt was a highly efficient catalyst for the hydrogen transfer reaction between isopropanol and cinnamaldehyde. Selectivity for cinnamic alcohol was higher than 99% and the conversion of cinnamaldehyde was higher than 95%. The regular morphology of the γ-Al_2O_3-nt support with homogeneous surface sites and the uniformly dispersed titanium oxide featured a high concentration surface Ti(III) species. These factors contributed to the high performance of the TiO_x/γ-Al_2O_3-nt catalyst.

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1. Introduction

Cinnamyl alcohol is an important fine chemical for high value applications, such as production of perfumes, flavors, and pharmaceuticals, and is typically manufactured by hydrogenation of cinnamaldehyde [1]. The hydrogenation of C=C in the C=C–C=O unit is more thermodynamically favorable than reduction of C=O. Thus, selective chemical reduction of the C=O group is a challenging synthetic transformation from both academic and industrial viewpoints [2]. Undesirable products such as hydrocinnamaldehyde or hydrocinnamyl alcohol are often formed in one- and two-step hydrogenation [3–5], leading to decreased selectivity of the unsaturated alcohol and increased purification costs. Thus, it is necessary to design more efficient catalysts that can facilitate selective hydrogenation of the C=O bond in the presence of other functionalities.

In general, supported catalysts based on transition metals (e.g., Pd, Pt, Ni, Cu or Au) are used for the hydrogenation of cinnamaldehyde [6–10]; however, the selectivity of such catalysts for the unsaturated alcohol is usually quite low. An alternative approach to reducing the C=O group by hydrogen transfer involves the use of a metal alkoxide as a catalyst and a secondary alcohol as a hydrogen donor. These processes are known as Meerwein-Ponndorf-Verley (MPV) reduction (Scheme 1) [11–17]. Traditional catalysts for MPV reduction are homogeneous catalysts based on aluminum, boron, and zirconium alkoxides [11–13]. However, these homogeneous catalysts feature problems, such as the need for a large amount of catalyst, environmentally unfriendly neutralization processes, and difficulty of isolating products and recycling/reusing

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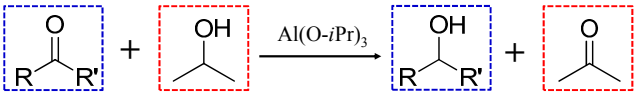

R = $(CH_3)_nCH=CH$; $C_6H_5CH=CH$; etc.
R' = CH_3; H; etc.

Scheme 1. General mechanism for the MPV reduction with Al(O-*i*Pr)$_3$.

the catalyst. These problems have lately been circumvented with the use of different heterogeneous catalysts. Many researchers have examined the performance of such catalysts, including metal oxides [18–20] or hydroxides [21], hydrotalcites [22–24], and various zeolites [25, 26]. However, these catalysts commonly show selectivity too low for practical use and also feature expensive post-synthesis separations. More efficient, selective, and stable heterogeneous catalysts for MPV reduction are highly desired.

Monoxides of metals such as Al_2O_3 [27] and TiO_2 [28] can be used as catalysts for MPV reduction; however, they are generally considered to be ineffective for intermolecular MPV reductions. Some recent reports have indicated that the selectivity for unsaturated alcohols can be improved with the use of partially reduced metal oxides, such as titanium oxide, because of the strong interaction between the carbonyl group and the positively charged catalytic center ($TiO_x^{\delta+}$) [29]. In this work, a series of catalysts, based on titanium oxide dispersed on alumina, are prepared and their catalytic performances are tested for the MPV reduction of cinnamaldehyde to cinnamyl alcohol. A nanotubular alumina that enabled titanium oxide to be stably dispersed over the alumina surface in a low valance state (denoted as TiO_x/γ-Al_2O_3-nt) showed excellent performance for the title reaction.

2. Experimental

2.1. Catalyst synthesis

Here, we used two types of Al_2O_3 as substrates with different morphologies. We synthesized γ-Al_2O_3 nanotubes by a hydrothermal method, with an alumina sol precursor. The precursor power (γ-AlOOH) was heated at a heating rate of 2 K/min to 873 K in air to obtain Al_2O_3 nanotubes. The as-prepared Al_2O_3 nanotubes were denoted as γ-Al_2O_3-nt. Commercial Al_2O_3, exhibiting an amorphous morphology was purchased from Aluminum Corporation of China Limited, and heated at 873 K for 8 h in air before use. The commercial Al_2O_3 was denoted as γ-Al_2O_3-c.

The TiO_x/γ-Al_2O_3 catalysts were prepared by a reactive deposition method, and TiO_2 nanoparticles were fabricated directly on the surface of the Al_2O_3. First, a certain amount of tetrabutyl titanate (TBOT) was dissolved in a 40-mL mixture of toluene (Aldrich) and ethanol (Aldrich) (*V*:*V* = 1:1) under magnetic stirring at room temperature. Then γ-Al_2O_3-nt or γ-Al_2O_3-c powder was slowly added to the mixture with magnetic stirring at room temperature for 24 h. The solid powder was then collected by centrifugation, washed several times with ethanol and dried in air at 353 K followed by grinding. The

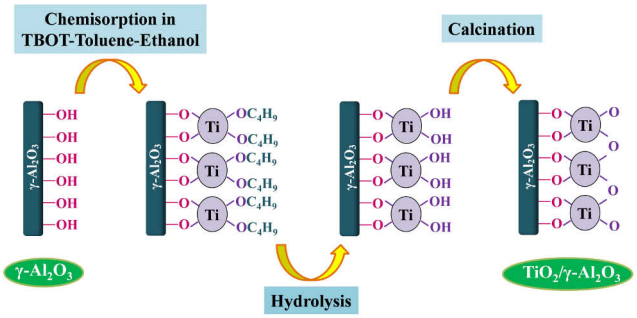

Fig. 1. Schematic illustration of the TiO_2/γ-Al_2O_3 catalyst preparation procedure.

fine powder was heated to 673 K under an air atmosphere for 4 h and then heated under an Ar atmosphere at the same temperature for 2 h to remove organic pollutants and produce stoichiometric TiO_2 on the surface of γ-Al_2O_3. In this way, the TiO_2/γ-Al_2O_3-nt and TiO_2/γ-Al_2O_3-c composites were prepared (Fig. 1). The composite was subsequently treated in H_2 (50 mL/min) at 873 K with a heating rate of 10 K/min for 2 h and cooled to room temperature under same atmosphere. Finally, the TiO_x/γ-Al_2O_3-nt and TiO_x/γ-Al_2O_3-c catalysts were obtained.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns were measured with a Phillips X'Pro diffractometer using Cu K_α radiation (λ = 0.15418 nm) at 40 kV and 25 mA in the 2θ range 10°–90°. The texture of the solids was calculated from nitrogen adsorption-desorption isotherms at liquid nitrogen temperature, which were recorded on a Micromeritics ASAP-2020 instrument. The chemical composition of the samples was determined by X-ray fluorescence spectrometry (XRF) with the use of an ARL-9800 instrument. Samples were out gassed in vacuo at 573 K for 6 h prior to use. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method. Transmission electron microscope (TEM) image was performed on a JEOL JEM-200CX at an accelerating voltage of 200 kV. The Raman spectra were recorded in the range of 150–800 cm^{-1} with a resolution of 4 cm^{-1} on a Renishaw Invia Raman microscope equipped with a Nd:YAG laser (λ = 532 nm).

For H/D exchange, the as-prepared samples (150 mg) were pretreated under Ar (40 mL/min) by heating to 873 K at 10 K/min and maintained at this temperature for 2 h. The sample was then cooled under the same atmosphere to room temperature. The exchange of protons for deuterium in the sample was measured by increasing the temperature to 873 K at a heating rate of 10 K/min. The signal of HD was monitored by mass spectrometry.

In situ X-ray photoelectron spectroscopy (XPS) measurements were conducted in a commercial XPS system (PHI 5000 Versa Probe) equipped with a hemispherical electron analyzer and monochromatic Al K_α X-ray excitation source. The sample was first evacuated at 393 K for 1 h, then cooled to room temperature, and the spectra were measured. Then the sample was reduced at 873 K under H_2 (30 mL/min) for 2 h. After the sam-

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