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Stabilizing cobalt catalysts for aqueous-phase reactions by strong metal-support interaction

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A B S T R A C T

High-temperature calcination and reduction treatments of cobalt particles (17–20 nm) supported on TiO_2 create cobalt particles covered with a TiO_y layer. The layer thickness ranges from 2.8 to 4.0 nm. These phenomena, commonly called strong metal-support interaction (SMSI), can be used to improve the catalyst stability and change the catalyst selectivity. For example, non-overcoated cobalt catalysts leached during aqueous-phase hydrogenation (APH) of furfuryl alcohol, losing 44.6% of the cobalt after 35 h time-on-stream. In contrast, TiO_y-overcoated cobalt catalysts did not lose any measurable cobalt by leaching and the cobalt particle size remained constant after 105 h time-on-stream. The 1,5-pentanediol selectivity from furfuryl alcohol hydrogenolysis increased with increasing TiO_y layer thickness. The stabilized cobalt catalyst also had high yields for APH of xylose to xylitol (99%) and APH of furfural to furfuryl alcohol (95%). These results show that the SMSI effect produces a catalyst with a similar structure as catalysts prepared by atomic layer deposition, thereby opening up a cheaper and more industrially relevant method of stabilizing base-metal catalysts for aqueous-phase biomass conversion reactions. In addition, the SMSI effect can be used to tune catalyst selectivity, thus allowing the more precise atomic scale design of supported metal catalysts.

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1. Introduction

Catalytic aqueous-phase hydroprocessing approaches can be used to produce a wide variety of liquid fuels and commodity chemicals from biomass [1–6]. Aqueous-phase processing has been primarily carried out with supported precious-metal catalysts. Dumesic and co-workers produced alkanes from aqueous-phase conversion of carbohydrates using Pt catalysts [7,8]. Alkanes can also be prepared from cellulose using Ir—Re and Ru catalysts [9,10]. Ru and Pt catalysts have been used for aqueous-phase hydrogenation of carbohydrates and organic acids [11–13].

Mono-functional organic compounds can be prepared from sugar alcohols using Pt—Re catalysts [14,15].

There have been efforts to use base-metal catalysts for these processes. It is generally known that base-metal catalysts leach and sinter under harsh aqueous conditions [16,17]. Sulfided Co—Mo catalysts have been used for hydrodeoxygenation of pyrolysis oils [18,19]. However, these catalysts deactivate due to coking and sulfur loss. Leaching of promoter metals (e.g., Mo) is another problem when using the Mo-modified catalysts [20]. Other authors have used base-metal catalysts for aqueous-phase conversion of lignin and cellulose in batch reactors [21,22]. Bimetallic Pt—Co nanoparticles in hollow carbon spheres were able to convert 5-hydroxymethylfurfural into 2,5-dimethylfuran in 98% yield [23]. However, the long term catalyst stability in these batch reactors was not determined. Raney Ni catalysts have also been used to upgrade bio-oils by hydrogen transfer reactions [24,25]. However, the Raney catalysts are known to undergo metal leaching [11,26,27]. Therefore, it would be highly desirable to stabilize inexpensive supported non-sulfide base-metal catalysts for the aqueous-phase processes.

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We have recently reported that base-metal catalysts can be stabilized by overcoating with a layer of Al_2O_3 or TiO_2 using atomic layer deposition (ALD) [28–30]. An Al_2O_3 overcoat formed by ALD stabilized the copper particles against leaching and sintering for liquid-phase hydrogenation reactions [28]. An ALD TiO_2 overcoated cobalt catalyst was resistant against leaching and sintering for aqueous-phase hydrogenation (APH) reactions where it was proposed that the TiO_2 selectively decorated defect and edge cobalt sites where leaching and sintering begin [29]. The ALD approach has also been used to stabilize Pd catalyst against coking and sintering for gas-phase ethane dehydrogenation at 948 K [31]. However, ALD is an expensive and time-intensive process to produce supported metal catalysts [32]. It would be highly desirable to prepare stabilized base-metal catalysts without using ALD technology. The so-called strong metal-support interaction (SMSI) effect has been reported to be due to migration of partially reduced metal oxide species onto the surface of metal particles [33–37]. Dumesic et al. monitored the changes in physical and chemical properties of a Ni—TiO_2 system during reaction in hydrogen using transmission electron microscopy (TEM) [38]. Zander et al. have recently observed the formation of a ZnO layer covering copper particles upon reduction by means of a depth-sensitive synchrotron X-ray photoelectron spectroscopy (XPS) [39]. The SMSI effect has been used to design catalysts for methanol synthesis on Cu-based catalysts [39], CO oxidation on Pd-based catalysts [40], hydrogen production on Pt-based catalysts [41], furfural hydrogenation on Pt-based catalysts [42], and CO and CO_2 hydrogenation on Co-based catalysts [43]. However, previous studies have focused on enhancing activity and/or selectivity for the gaseous-phase reactions.

Herein, we show that the SMSI effect can be used to stabilize a Co/TiO_2 catalyst under aqueous-phase reaction conditions. High-temperature calcination and reduction treatments of a Co/TiO_2 catalyst create overcoats of TiO_y on cobalt particles by SMSI, protecting the cobalt particles against leaching and sintering in the aqueous phase. The SMSI effect also creates bifunctionality in the Co/TiO_2 system, which can be used to produce value-added commodity chemicals from renewable feedstocks. This is the first report of a highly stable and selective supported base-metal catalyst prepared using SMSI for aqueous-phase hydrogenation and hydrogenolysis of oxygenates.

2. Experimental

2.1. Catalyst preparation

A commercial P25 TiO_2 (surface area = 51 $m^2 g^{-1}$, Aldrich) was calcined at 1023 K (4 K min^{-1}) for 4 h. The calcined TiO_2 (surface area = 10.2 $m^2 g^{-1}$) was used as the support. The cobalt nitrate precursor (Co$(NO_3)_2$·6H_2O; Sigma–Aldrich, ⩾98%) was added to the TiO_2 support using incipient wetness impregnation. After impregnation, the catalyst was dried at 373 K for 12 h. The prepared Co/TiO_2 catalyst was calcined to remove the nitrates in a 1st calcination step in air at 573 K (1 K min^{-1}) for 2 h. Cobalt loading of the Co/TiO_2 was 4.96 wt% as measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

A batch of the Co/TiO_2 catalyst was directly reduced at temperatures of 723 and 873 K, without a 2nd calcination treatment. They are denoted as Co/TiO_2 723 R and Co/TiO_2 873R. A second batch of the Co/TiO_2 catalyst was calcined at 673 K (i.e., 2nd calcination at 673 K) and then reduced at different temperatures of 723 and 873 K, labeled as Co/TiO_2 673C-723R and Co/TiO_2 673C-873R respectively. A third batch of the Co/TiO_2 catalyst was calcined at 873 K (i.e., 2nd calcination at 873 K) and then reduced at 873 K, called Co/TiO_2 873C-873R.

2.2. Catalyst characterization

Scanning transmission electron microscopy (STEM) was carried out using a C_s-corrected FEI Titan microscope operated at 200 kV. HAADF STEM images were collected with a 24.5 mrad probe semi-angle and ~25 pA probe current. To prepare the samples for STEM, the catalysts were suspended in ethanol, ultrasonicated for 5 min and then deposited on a carbon-coated copper grid. STEM samples were plasma cleaned for 20 min before loading into the microscope. Particle size of the catalysts was obtained using a Tecnai T12 TEM at 120 kV. About 200 particles were analyzed for each particle size distribution measurement. Prior to STEM and TEM imaging, the samples were passivated in 10% oxygen after reduction.

Static hydrogen chemisorption was carried out using a Micromeritics ASAP 2020 system. Before hydrogen chemisorption, samples were reduced in situ under hydrogen flow at 723 or 873 K (1 K min^{-1}), held for 2 h, purged with helium for 2 h, evacuated for 140 min, and cooled down to 308 K. Hydrogen was dosed on the catalyst at 308 K until the equilibrium pressure was 560 mmHg to determine the total amount of adsorbed hydrogen. The hydrogen in the cell was then evacuated. After the evacuation, hydrogen was again dosed on the catalyst to determine the amount of weakly adsorbed hydrogen. The amount of strongly adsorbed hydrogen was determined by subtracting the weakly adsorbed hydrogen from the total adsorbed hydrogen.

Brunauer–Emmett–Teller (BET) surface area was calculated from nitrogen adsorption data at 77 K obtained using the Micromeritics ASAP 2020 system. Before BET measurements, samples were degassed under vacuum at 523 K.

Temperature-programmed reduction (TPR) was carried out using a Micromeritics AutoChem II 2920 unit. Before TPR, samples were pretreated in helium at 423 K for 30 min. A TPR run was carried out in a flow of 10% hydrogen/argon mixture gas at a flow rate of 50 mL min^{-1} with a temperature ramp of 10 K min^{-1}. A dry ice/acetone cooling bath removed moisture from the TPR effluent stream at 195 K before the stream entering a thermal conductivity detector (TCD). The consumption of hydrogen was monitored using the TCD and quantified based on hydrogen consumption of a TPR standard.

X-ray diffraction (XRD) analyses were performed using a Rigaku D/Max Rapid II diffractometer with a Mo Kα source in the scan range from 5° to 45° at a scan rate of 0.02° s^{-1}. Samples were put in thin-wall glass capillaries. Diffraction data were collected on a 2-D image-plate detector. The two-dimensional images were then integrated to produce conventional 2θ vs. intensity patterns using Rigaku's 2DP software. Peak identification was carried out using Jade 9 software. Prior to XRD, the samples were passivated in 10% oxygen after reduction.

The cobalt loading of catalysts before and after reaction was analyzed by ICP-AES using a Perkin-Elmer Plasma 400 ICP Emission Spectrometer. A catalyst (10 mg) was digested with a mixture of 1 mL nitric acid (Fisher, 69.2 wt%), 3 mL hydrochloric acid (Fisher, 37.4 wt%), and 5 mL hydrofluoric acid (Acros Organics, 48–51%) in a Teflon beaker at 383 K for 24 h. Cobalt standards for the ICP analysis were prepared from a cobalt ICP standard (Fluka, 1000 ± 2 mg L^{-1}).

Raman experiments were carried out with a high-performance Renishaw InVia Raman Spectrometer with a 514 nm (excitation) laser. This is a Modu-Laser Stellar-REN with an output of 50 mW and an approximate power of 15–20 mW at the sample. All measurements used a 2400 l mm^{-1} grating with an efficiency of approximately 30% at 514 nm. In situ Raman studies used an Olympus LMPlanFL N objective with 50× magnification and a working distance of 10.6 mm. Scattered light was filtered into a UV enhanced (lumogen coated) deep depleted array detector