Stabilizing Cobalt Catalysts for Aqueous-Phase Reactions by Strong Metal-Support Interaction

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Abstract: High-temperature calcination and reduction treatments of cobalt particles (17 to 20 nm) supported on TiO_2 create encapsulated cobalt particles with a TiO_y layer. The layer thickness ranges from 2.8 to 4.0 nm. This encapsulation, 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 hour time-on-stream. In contrast, encapsulated cobalt catalysts did not lose any measurable cobalt by leaching and the cobalt particle size remained constant after 105 hour 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.

Keywords: Strong metal-support interaction; biomass conversion; cobalt; TiO_2 ; atomic layer deposition

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.

We have recently reported that base-metal catalysts can be stabilized by overcoating with a layer of Al₂O₃ or TiO₂ using atomic layer deposition (ALD) [28-30]. An Al₂O₃ overcoat formed by ALD stabilized the copper particles against leaching and sintering for liquid-phase hydrogenation reactions [28]. An ALD TiO₂ 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 begins [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_x 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 values-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 TiO₂ (surface area = 51 m² g⁻¹, Aldrich) was calcined at 1023 K (4 K min⁻¹) for 4 hours. The calcined TiO₂ (surface area = 10.2 m² g⁻¹) was used as the support. The cobalt nitrate precursor (Co(NO₃)₂·6H₂O; Sigma-Aldrich, • 98 %) was added to the TiO₂ support using incipient wetness impregnation. After impregnation, the catalyst was dried at 373 K for 12 hours. The prepared Co/TiO₂ catalyst was calcined to remove the nitrates in a 1st calcination step in air at 573 K (1 K min⁻¹) for 2 hour. Cobalt loading of the Co/TiO₂ was 4.96 wt% as measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

A batch of the Co/TiO₂ catalyst was directly reduced at temperatures of 723 and 873 K, without a 2nd calcination treatment. They are denoted as Co/TiO₂ 723 R and Co/TiO₂ 873R. A second batch of the Co/TiO₂ 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/TiO₂ 673C-723R and Co/TiO₂ 673C-873R respectively. A third batch of the Co/TiO₂ catalyst was calcined at 873 K (*i.e.*, 2nd calcination at 873 K) and then reduced at 873 K, called Co/TiO₂ 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 semiangle and ~25 pA probe current. To prepare the samples for STEM, the catalysts were suspended in ethanol, ultrasonicated for 5 minutes and then deposited on a carbon-

coated copper grid. STEM samples were plasma cleaned for 20 minutes 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 hours, purged with helium for 2 hours, evacuated for 140 minutes, 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 minutes. 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 K source in the scan range from 5 to 45° at a scan rate of $0.02^\circ\text{ sec}^{-1}$.

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 2 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 hours. 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 50x magnification and a working distance of 10.6 mm. Scattered light was filtered into a UV enhanced (lumogen coated) deep depleted array detector (Renishaw). The laser line was calibrated with a Ne calibration lamp under the Full Calibration technique to match the calibration wavenumbers and intensities to the collected values. In addition to calibrating the laser, the Raman spectrograph was calibrated to an internal Si standard at 520.7 cm⁻¹. Raman measurements were taken with a range of 100-1200 cm⁻¹ and a dispersion of 1.36565 cm⁻¹ pixel⁻¹. *In situ* measurements were taken with a fully open aperture and a 10 seconds exposure time. Approximately 10 mg of sample was used for each *in situ* trial. Experiments were performed in a high-temperature cell (Linkam CCR1000) designed for temperatures up to 1273 K. This setup used a quartz window and water-cooled O-rings. The

temperature was controlled by a Linkam T95-HT system. Gas flows during *in situ* experiments were controlled by mass flow controllers (Bronkhorst EL-Flow) with maximum flow rates of 50, 100, and 40 mL min⁻¹ for hydrogen, helium, and oxygen, respectively. The mass flow controllers were directed by a digital readout system (Bronkhorst series E-7000) capable of mixing gases with variable flow rates. A flow rate of 10 mL min⁻¹ hydrogen (Airgas, Ultra High Purity) was used for all reductions, and 20 mL min⁻¹ of a 20 % oxygen/helium (Airgas, Ultra High Purity) mixture was used for all calcinations. Heating ramps for *in situ* reductions and calcinations were kept at 1 and 5 K min⁻¹, respectively, as was the case in reactivity treatments. Once the desired temperature was reached, it was held there for two hours. The sample was cooled to room temperature after calcination and reduced with a 1 K min⁻¹ heating ramp for spectra that required calcination prior to reduction. Spectra used in this study were taken at room temperature under 16 mL min⁻¹ helium flow after the calcination and/or reduction was complete. Raman spectra were fitted using Fityk 0.9.8. The background was first subtracted from each spectrum. The resulting spectra were normalized to the area of the A_{1g} signal of TiO₂ (615 cm⁻¹). The 340, 400, and 440 cm⁻¹ signals were then deconvoluted. Each signal was fitted with a Gaussian curve. Areas were calculated by the equation, Area = 2 × *hwhm* × height, where *hwhm* is the half-width at half-maximum.

2.3. Catalyst testing in a continuous flow reactor

Aqueous-phase hydrogenation and hydrogenolysis reactions were performed in a stainless-steel tubular reactor (6.35 mm outer diameter and 5.46 mm inner diameter), heated by a furnace (Lindberg). Feedstocks were furfuryl alcohol (Sigma-Aldrich, • 98 %), furfural (Sigma-Aldrich, 99 %), and xylose (Acros Organics, 99+ %). A uniform temperature profile along the catalyst bed was achieved using aluminum filler inserted in the void between the furnace and the

tubular reactor. We ran a blank reaction without catalyst to confirm that there is no homogeneous reaction and no effect of the reactor materials. For catalyst testing, 0.5 g of a catalyst without diluents was loaded into the reactor with quartz wool and cylindrical quartz beads packed on both sides. Weight hourly space velocity (WHSV) was calculated by $\text{WHSV} = \text{hourly mass liquid feed flow rate (g/h)} / \text{catalyst mass (g)}$. Before a reaction, in case of Co/TiO₂ 873C-873R, a Co/TiO₂ catalyst was calcined *in situ* in air (Airgas, Grade D) of 100 mL min⁻¹ at 873 K (5 K min⁻¹) for 2 hours, purging with helium (Airgas, Industrial Grade) at ambient temperature for 30 minutes, followed by reduction in hydrogen (Airgas, Ultra High Purity) of 100 mL min⁻¹ at 873 K (1 K min⁻¹) for 2 hours. After the reduction was complete, the furnace was cooled to the desired reaction temperature and the reactor system was pressurized to 2.34 MPa using a back-pressure regulator. A 2 wt% aqueous feedstock solution was then fed to the reactor using a high-performance liquid chromatograph (HPLC) pump (Varian ProStar), co-fed with hydrogen (Airgas, Ultra High Purity) of 40 mL min⁻¹. A 150 mL gas-liquid separator was used to accumulate liquid products at the top of the reactor. Gaseous products continued to flow to the back-pressure regulator to maintain the reaction pressure. Both an excess flow shut-off valve and a pressure relief valve were installed in the reactor system to ensure safe operation. The gaseous products were analyzed using an online gas chromatograph (GC; Shimadzu GC-2014) with a flame ionization detector (FID) fitted with a Rt®-Q-Bond (Restek) capillary column and a TCD fitted with a GS-CarbonPLOT (Agilent) column. A liquid sample accumulated in the gas-liquid separator was drained periodically into a collecting container, followed by being filtered through a 0.2 µm syringe filter. The liquid products were analyzed using a GC (Shimadzu GC-2010) with a FID fitted with a Rtx®-VMS (Restek) capillary column and a HPLC (Shimadzu LC-20AT) with a refractive index detector (RID) fitted with an Aminex® HPX-87H column (Bio-Rad). Total organic carbon (TOC) measurements were performed using a Shimadzu TOC-VCPH

Analyzer for the liquid samples obtained from the reaction to measure the overall carbon balance. TOC calibrations were performed with carbon standards (SpectroPure).

3. Results and discussion

3.1. Catalyst characterization

Figure 1(a) and (b) show cobalt metal particles are covered by a thin layer that is blurry on the fringes of the cobalt particle. The blurriness is not observed with pure metallic particles indicating that a TiO_2 layer is forming over the cobalt catalysts. Figure 1(c) depicts the decoration of metallic cobalt nanoparticle by a TiO_2 layer as striations. It also shows cobalt metal sites are assessable despite the decoration. The reason for the overcoating is not clear, but is likely thermally induced [43]. The thickness of the layer can be measured from the STEM images. Adding a 2nd calcination step caused a statistical significantly increase (95 % confident limit using the student's *t*-test) in the size of the layer from 2.8 ($\pm$ 0.18) nm for the Co/ TiO_2 873R catalyst to 3.5 ($\pm$ 0.2) nm for the Co/ TiO_2 673C-873R catalyst. Increasing the 2nd calcination temperature from 673 to 873 K also significantly increased the size of the layer from 3.5 ($\pm$ 0.2) to 4.0 ($\pm$ 0.15) nm. Chemisorption results presented in Table 1 showed that the catalyst does adsorb hydrogen even after calcination and reduction at 873 K. This indicates that the cobalt surface sites are still accessible despite the overlayer.

Figure 1. STEM images of (a) Co/TiO₂ 873R, (b) Co/TiO₂ 673C-873R, and (c) Co/TiO₂ 873C-873R.

Table 1. Cobalt particle size, dispersion, hydrogen uptake, and BET surface area of the Co/TiO₂ catalysts with different treatments.

Catalyst	Cobalt particle size ^(a) (nm)	Dispersion ^(b) (%)	Hydrogen uptake ^(c) (μmol H g ⁻¹)	Dispersion ^(d) (%)	BET surface area (m ² g ⁻¹)
Co/TiO ₂ 723R	17.0 (± 5.4)	6.3 (± 2.1)	16.70	4.7	10.7
Co/TiO ₂ 673C-723R	17.6 (± 5.3)	6.1 (± 1.9)	11.88	6.3	11.4
Co/TiO ₂ 873R	17.7 (± 5.4)	6.1 (± 1.9)	15.58	4.4	10.8
Co/TiO ₂ 673C-873R	18.8 (± 5.7)	5.7 (± 1.8)	10.28	5.4	11.7
Co/TiO ₂ 873C-873R	20.2 (± 6.2)	5.3 (± 1.7)	7.38	3.9	11.8

^(a)Cobalt particle size measured by TEM

^(b)Cobalt dispersion estimated based on cobalt particle size measured by TEM

^(c)Strongly adsorbed hydrogen uptake determined by static hydrogen chemisorption

^(d)Cobalt dispersion estimated based on hydrogen uptake and extent of reduction

The cobalt particle size of the Co/TiO₂ catalyst as measured by TEM ranged from 17 ($\pm$ 5.4) to 20.2 ($\pm$ 6.2) nm (Table 1 and Figure S1). The cobalt particle size of the Co/TiO₂ 723R and the Co/TiO₂ 673C-723R were not significantly different based on student's *t*-test at 95 % confident limit. In the case of the Co/TiO₂ 873R and the Co/TiO₂ 673C-873R, there was also no statistically significant change in the cobalt particle size. However, there was a statistically significant difference in the cobalt particle size between the Co/TiO₂ 673C-873R and the Co/TiO₂ 873C-873R. The particle size growth during the 2nd calcination at 873 K is due to agglomeration of cobalt [44]. The hydrogen uptake decreased with an increase in calcination temperature. This is mainly due to the TiO_y species covering cobalt sites. This is similar to our previous results that showed a decrease in hydrogen uptake when a TiO₂ overcoat was added to a Co/TiO₂ catalyst by ALD [29]. The cobalt dispersion estimated from the cobalt particle size matches with the dispersion estimated from hydrogen uptake and the extent of reduction (Table 1).

Increasing the calcination temperature caused the cobalt to reduce at higher temperature, as shown in Figure 2. Table 2 shows the extent of reduction of the Co/TiO₂ catalyst as a function of different calcination conditions. As shown by XRD analysis (see Figure S2), Co₃O₄ exists in the catalyst before reduction, regardless of the calcination temperature. Only 20 to 40 % of Co₃O₄ was reduced to metallic Co, as shown in Table 2. This means that a large fraction of the Co is irreducible, even at 1000 K. However, *in situ* Raman spectroscopy, a surface-sensitive technique, shows the cobalt on the surface was completely reduced at 723 K (Figure 3(iii)). This indicates that the unreduced cobalt is located in the core of the cobalt particles, not on the surface. The extent of reduction of the Co/TiO₂ decreased with increasing calcination temperature (Table 2). The decrease in the extent of reduction and shift in reduction peaks indicates that an interaction between cobalt oxide and support exists at increasing calcination temperature [37, 45]. The

extent of reduction decreased when a TiO_2 was overcoated by ALD over the surface of a Co/TiO_2 catalyst [29]. The hydrogen chemisorption and TPR results indicate that the TiO_2 decoration of cobalt particles by SMSI and ALD are similar.

Figure 2. TPR patterns of the Co/TiO_2 after different 2nd calcination temperatures. (a) No 2nd calcination, (b) 2nd calcination at 673 K, and (c) 2nd calcination at 873 K.

Table 2. Reducibility and hydrogen consumption of the Co/TiO_2 with different calcination treatments determined by TPR measurements.

Catalyst	Extent of reduction ^(a)
Co/TiO_2 without 2 nd calcination	41.7 % (420 - 710 K)
Co/TiO_2 after 2 nd calcination at 673 K	22.4 % (480 - 710 K)
Co/TiO_2 after 2 nd calcination at 873 K	22.3 % (480 - 900 K)

^(a)Extent of reduction based on hydrogen consumption from TPR and theoretical hydrogen consumption assuming that Co_3O_4 is completely reduced to Co.

The TiO_2 support and the Co/TiO_2 catalyst before the 2nd calcination and reduction were analyzed by Raman spectroscopy and XRD. Figure 3(i) shows the Raman spectrum of the TiO_2

support. The 440 and 615 cm^{-1} bands represent the rutile phase of TiO_2 [46]. The intensities of these bands relative to the 140 cm^{-1} anatase band [46] show that the TiO_2 support is composed primarily of rutile. The XRD pattern of the TiO_2 support also confirms that the TiO_2 support is composed of rutile (see Figure S2(i)).

The spectrum of the Co/TiO_2 before the 2nd calcination and reduction is shown in Figure 3(ii). The peaks at 190, 480, 520, and 685 cm^{-1} indicate that Co_3O_4 exists in the catalyst [47]. As we discussed above, the XRD also shows the Co_3O_4 phase in this material (see Figure S2(ii)). After calcination at 873 K, the Co_3O_4 still exists in the catalyst, as shown in Figure S2(iii). In Figure 3(iii)-(viii), no Co_3O_4 signals (*i.e.*, no peaks at 190, 480, 520, and 685 cm^{-1}) were observed after reduction at temperatures of 723 and 873 K. We emphasize that Raman spectroscopy is a surface-sensitive technique and cannot detect species in the metallic state. Thus, this indicates that Co_3O_4 is reduced to its metallic phase above 723 K on the catalyst surface.

New Raman signals at 340 and 400 cm^{-1} appear in Figure 3(iii)-(v). These 340 and 400 cm^{-1} signals do not match with either cobalt titanate (CoTiO_3) or cobalt (II) oxide (CoO), as shown in Figure 4. Moreover, Figures S3 and S4 show that CoTiO_3 is essentially unreducible under the 873 K reduction treatment that is carried out in Figure 3(vi)-(viii). However, the samples producing the spectra (vi) to (viii) in Figure 3 are reduced at 873 K (*i.e.*, no 340 and 400 cm^{-1} signals in Figure 3(vi)-(viii)), so CoTiO_3 is not formed during the 2nd calcination and reduction treatments of the Co/TiO_2 .

Figure 3. Raman spectra of Co/TiO₂ with different calcination and reduction temperatures. Spectra (iii) to (viii) were obtained by being treated *in situ* at different temperatures (○ TiO₂ rutile; □ Co₃O₄).

Figure 4. Comparison of Raman spectrum of the Co/TiO₂ catalysts, CoTiO₃ (Alfa Aesar, 99.8 %), and CoO (Acros Organics, > 99 %).

We attribute the 340 and 400 cm⁻¹ signals to TiO_y migration onto cobalt, namely SMSI. High-temperature calcination leads to SMSI, which can form new bonds between Co, O, and Ti, creating new Raman signatures at 340 and 400 cm⁻¹. Figure 3(ii) does not show these signals while they are clearly visible in Figure 3(iii). High temperature calcination and reduction did not

change the BET surface area or TiO_2 support phase of the catalyst. This means the phase change of the TiO_2 support is not needed for SMSI effect occurring on the catalyst surface, as shown in Table 1 and Figure S2 respectively [33]. Figure 3 shows the persistence of TiO_2 signals after the calcination and reduction treatments up to 873 K. These observations suggest that the 340 and 400 cm^{-1} Raman signals are not due to changes in the TiO_2 support but due to the interaction between cobalt and TiO_2 .

Figure 5 shows the relative peak area of the 340 and 400 cm^{-1} signals with different calcination temperatures. Fitting parameters for these signals are provided in Table S1. The area of the 340 cm^{-1} signal increases slightly with increasing calcination temperature from 573 to 673 K and then decreases with increasing calcination temperature from 673 to 873 K. TiO_y layers are formed over Co_3O_4 ($\text{Co}_3\text{O}_4\text{-TiO}_y$) during the 573 and 673 K calcinations, and this is then partially reduced to a $\text{CoO}_x\text{-TiO}_y$ species under 723 K reduction, which gives rise to the 340 cm^{-1} signal. The decrease in the intensity of the 340 cm^{-1} signal with further increase in calcination temperature is due to the fact that multiple layers of TiO_y may cover up these sites, making them invisible with surface-sensitive Raman spectroscopy. Therefore, this signal is attributed to the Co-O-Ti bond on top of a cobalt particle. This interaction requires some high-temperature treatment to be created, but is covered up by additional TiO_y layers with higher-temperature calcination.

The area of the 400 cm^{-1} signal decreases with increasing calcination temperature (Figure 5). We attribute this signal to interfacial sites on partially reduced CoO_x covered by TiO_y species (Co-O-Ti bond). In the 340 cm^{-1} case, the environment directly below the surface of the bond is a cobalt particle. However, in the 400 cm^{-1} case, the environment directly below the bond is the TiO_2 support, as this signal is brought about at the particle edges. The decrease in area of this signal is due to multiple layers of TiO_y covering the Raman-active species, as was the case for

the decrease in area of the 340 cm^{-1} signal with 873 K calcination. This decrease in area occurs at lower calcination temperatures for the 400 cm^{-1} signal because the covering of the interfacial sites by TiO_y is easier than the migration of TiO_y over the top of a Co_3O_4 particle.

These findings are supported by Weckhuysen *et al.*, who found that Co/TiO_2 was not completely reduced to Co^0 after reduction at 728 K [48]. The same paper also concluded that two different levels of Co-support interaction existed on the catalyst. This provides further evidence towards the assignment of the 340 and 400 cm^{-1} signals to different surface species.

Figure 5 also shows the behavior of the 440 cm^{-1} (rutile) signal with increasing calcination temperature. We can see that this peak has relatively constant area, in comparison to the 340 and 400 cm^{-1} signals. This was expected, as we have already stated that BET showed no structural changes in TiO_2 with 873 K calcination. Therefore, the constant area of the 440 cm^{-1} signal supports the accuracy of the deconvolution of the overlapping 400 and 440 cm^{-1} signals.

Figure 5. Relative peak area of 340 , 400 , and 440 cm^{-1} signals with increasing calcination temperature while holding reduction temperature constant at 723 K (■ 340 cm^{-1} ; ■ 400 cm^{-1} ; ■ 440 cm^{-1}). All spectra were normalized to the 615 cm^{-1} rutile peak.

The 340 and 400 cm^{-1} signals appear to be due to the TiO_y overlayer on the Co_3O_4 . The intensity of these signals depended on calcination temperature, showing that higher-temperature calcination leads to thicker TiO_y layers over Co. These signals are not visible in the samples reduced at 873 K (Figure 3(vi)-(viii)), indicating that the Co_3O_4 - TiO_y species formed with high-temperature calcination is reduced to its metallic state (Co- TiO_y) at 873 K (again, metallic species are not visible by Raman spectroscopy). The *in situ* Raman spectroscopy results are consistent with the STEM and TPR work that indicate the overcoating of cobalt particles with a TiO_2 layer.

Figure 6 is a model of what suggest occurs during the encapsulation of the cobalt particles. The cobalt particles exposed on the surface are reduced (as indicated by Raman spectroscopy) while the bulk of the particles remains oxidized (as indicated by TPR). Oxidized TiO_y species migrate onto Co_3O_4 particles during high-temperature calcination, forming Co_3O_4 - TiO_y species. Increasing the calcination temperature gives a strong interaction between the cobalt and TiO_2 , increasing the TiO_y layer thickness. A high-temperature reduction treatment can reduce the Co_3O_4 - TiO_y to Co- TiO_y . The size of the TiO_y layer is greatly influenced by the treatment conditions.

Figure 6. A model of the Co/ TiO_2 system before and after calcination and reduction treatments.

3.2. Catalyst testing

The catalytic properties of the Co/TiO₂ with different treatments were studied for APH of furfuryl alcohol, furfural, and xylose. These are all key platform renewable non-petroleum based molecules [49, 50]. Hydrogenation of furfuryl alcohol and furfural has been studied using Pt, Pd, and Ru catalysts [51-55]. Hydrogenation of carbohydrates (*e.g.*, xylose to xylitol) is an industrial process using Ru catalysts [11]. Precious-metal catalysts have been used for all the reactions. Thus, hydrogenation of furfuryl alcohol, furfural, and xylose would benefit from stabilizing inexpensive cobalt catalysts.

The deactivation of the Co/TiO₂ 873C-873R catalyst during the APH of furfuryl alcohol in a continuous flow reactor is shown in Figure 7. Deactivation by coke formation on the catalyst is reversible upon calcination, while deactivation by leaching or sintering of cobalt is irreversible. The catalytic activity was able to be regenerated by calcination/re-reduction treatments, which suggests that no irreversible deactivation such as leaching and sintering occurred on the catalyst. No statistical difference in cobalt particle size of this catalyst was observed after 105 hour time-on-stream with a cobalt particle size of 20.2 ± 6.2 nm before reaction and 19.3 ± 5.4 nm after reaction (see Figure S1e-g). Furthermore, there was no change in the cobalt loading of the Co/TiO₂ 873C-873R catalyst before and after the reaction and regeneration cycles, as measured by ICP-AES (Figure 8). Also, no cobalt was detected in each liquid sample we ran for each of the different catalysts reduced at 873 K. However, up to 44.6 % of the cobalt leached from the Co/TiO₂ 723R catalyst after 42 hour time-on-stream. In addition, as shown in Table 3, the carbon balance for the Co/TiO₂ catalysts reduced at 723 K was less than 69 % whereas the one for the Co/TiO₂ catalysts reduced at 873 K was higher than 85 %. This suggests that treatments at high temperatures (*e.g.*, 873 K) prevent leaching, sintering, and coking. As inferred from *in situ* Raman spectroscopy, STEM, and hydrogen chemisorption, Co⁰ particles are decorated by a TiO_y species formed with reduction at 873 K. These results suggest

that reduced cobalt particles in contact with TiO_y are required to stabilize the cobalt particles under aqueous conditions. The TiO_y layers formed by SMSI could preferentially decorate under-coordinated defect and edge sites of cobalt atoms which is where leaching, sintering, and coking begin [56-58].

Figure 7. TOF for the APH of furfuryl alcohol as a function of time-on-stream and number of regenerations at 413 K, 2.34 MPa, and WHSV = 94 h^{-1} using the Co/TiO_2 873C-873R (■ fresh; ● one regeneration; ▲ two regenerations). Furfuryl alcohol conversion varied between 9.3 and 19.5 %. Regeneration of the catalyst was carried out by calcining the catalyst at 873 K and then re-reducing the catalyst at 873 K.

Figure 8. Cobalt leaching of the Co/TiO₂ catalysts after reaction.

Table 3. Molar carbon selectivity for the APH of furfuryl alcohol using the Co/TiO₂ with different treatment conditions. Reaction conditions: 413 K, 2.34 MPa, and WHSV = 5.8 h⁻¹.

Catalyst	Co/TiO ₂ 723R	Co/TiO ₂ 673C-723R	Co/TiO ₂ 873R	Co/TiO ₂ 673C-873R	Co/TiO ₂ 873C-873R
Conversion (%)	59.4	99.6	99.7	99.4	99.0
Selectivity (%)					
1,5-pentanediol	0	4.5	17.5	19.3	30.3
1,2-pentanediol	0	0.9	2.5	2.3	2.4
1,4-pentanediol	0	6.6	6.0	7.9	2.1
tetrahydrofurfuryl alcohol	0.3	2.5	11.9	7.8	20.7
cyclopentanone	45.8	2.2	0.6	0.4	0.5
cyclopentanol	0.6	28.6	12.2	11.1	5.2
1,3-cyclopentandiol	2.1	6.7	5.5	5.4	1.6
2-methylfuran	0.1	0.5	2.5	3.9	4.6
methane	0	0.02	0.1	0.1	0.6
1-butanol	0	0.2	1.2	1.2	1.5
1-pentanol	0	1.2	2.5	2.5	2.1
2-pentanol	0	0.9	1.6	1.7	1.4
undetected liquid carbon ^(a)	4.5	14.1	21.7	21.4	23.6
Carbon balance ^(b) (%)	53.4	68.9	85.8	85.0	96.6
Time-on-stream (h)	35.4	35.3	37.5	37.9	43.9

^(a)Undetected liquid carbon is the difference between moles of liquid carbon measured by TOC analyzer and moles of liquid carbon measured by GC-FID.

^(b)Carbon balance is the sum of moles of liquid carbon measured by TOC analyzer and moles of gaseous carbon measured by GC-FID/TCD.

One of the main products from APH of furfuryl alcohol over the Co/TiO₂ catalysts reduced at 873 K (*i.e.*, Co/TiO₂ 873R, Co/TiO₂ 673C-873R, and Co/TiO₂ 873C-873R) was 1,5-pentanediol (Table 3). 1,5-Pentanediol is a valuable commodity chemical that could potentially be used to make polyurethanes and polyesters [59]. 1,5-Pentanediol can be produced via selective hydrogenolysis of tetrahydrofuran (THF) ring which occurs on bifunctional catalysts [60] (*e.g.*, hydrogenolysis of tetrahydrofurfuryl alcohol (THFA)) using noble-metal catalytic systems such as Rh-Re, Pd-Ir-Re, or Rh-Ir-Re [60-63]. No product was observed when THFA was used as the feed over the Co/TiO₂ catalysts. Thus, 1,5-pentanediol is produced not by hydrogenolysis of THF ring but by hydrogenolysis of furan ring of furfuryl alcohol over the Co/TiO₂ catalysts. As shown in Table 3, the Co/TiO₂ 873R catalyst had 17.5 % selectivity toward 1,5-pentanediol. The Co/TiO₂ 673C-873R had 19.3 % 1,5-pentanediol selectivity. The 1,5-pentanediol selectivity increased from 19.3 to 30.3 % with increasing calcination temperature from 673 to 873 K (then reduced at 873 K). Nevertheless, the Co/TiO₂ 723R catalyst made no 1,5-pentanediol and the Co/TiO₂ 673C-723R produced 1,5-pentanediol but with low selectivity (4.5 %). These experimental results indicate that both calcination and reduction temperatures of Co/TiO₂ have a strong effect on 1,5-pentanediol production from furfuryl alcohol. Based on the experimentally observed hydrogenolysis selectivity trends, we hypothesize that the SMSI effect forms bifunctional sites that are present at the Co-TiO_y interface. These bifunctional sites facilitate hydrogenolysis of C-O-C bond of furan ring, which give rise to high selectivity toward 1,5-pentanediol. The 1,5-pentanediol yield from furfuryl alcohol hydrogenolysis over the Co/TiO₂ 873C-873R remained after three cycles of calcination/reduction treatments, as shown in Figure 9. These results suggest that SMSI can be used to control the relative rates of hydrogenation/hydrogenolysis reactions of supported metal catalysts.

Figure 9. Molar carbon yield as a function of time-on-stream for the conversion of furfuryl alcohol to 1,5-pentanediol at 413 K, 2.34 MPa, and WHSV = 5.8 h⁻¹ using the Co/TiO₂ 873C-873R. Dashed line represents regeneration. Regeneration of the catalyst was carried out by calcining the catalyst at 873 K and then re-reducing the catalyst at 873 K.

The APH of furfuryl alcohol produced several different products other than 1,5-pentanediol as shown in Scheme 1. THFA is produced via hydrogenation of the C=C bond of furan ring of furfuryl alcohol. 1,2-Pentanediol is converted from furfuryl alcohol via hydrogenolysis of C-O-C bond which occurs mostly on metal sites [64] whereas 1,5-pentanediol is produced on bifunctional sites [60]. 1,4-Pentanediol can be produced from isomerization of 1,2-pentanediol [65]. Ring rearrangement of furfuryl alcohol makes hydroxy-cyclopentenone as an intermediate in water [66, 67]. Hydrogenation of C=C and C=O bonds of the intermediate occurring on metal sites can produce 1,3-cyclopentanediol. The intermediate also undergoes hydrogenolysis of C-OH bond and hydrogenation of C=C bond, thereby produces cyclopentanone [67]. Cyclopentanol is produced through hydrogenation of C=O bond of the cyclopentanone [67]. 2-Methylfuran can be produced through hydrogenolysis the C-OH bond of furfuryl alcohol which has been reported to occur on metal sites of the catalysts [68]. 1-Pentanol and 2-Pentanol are formed in a ring-opening reaction of the furan ring of the 2-methylfuran [68].

When the 2-pentanol undergoes C-C bond cleavage reactions on metal sites [54], it produces 1-butanol and methane.

Scheme 1. Proposed reaction pathways for the APH of furfuryl alcohol over the Co/TiO₂.

The Co/TiO₂ 873C-873R catalyst was also selective for other APH reactions. It had 99.1 % xylitol yield for the APH of xylose at 373 K, as shown in Figure 10a. After the APH of xylose, the catalyst was regenerated and then tested for the APH of furfural. As shown in Figure 10b, furfural was converted into furfuryl alcohol with 95.4 % yield at 353 K. These results demonstrate that the Co/TiO₂ 873C-873R catalyst was highly selective for hydrogenation of carbonyl compounds to the corresponding alcohols which is an important reaction for biomass conversion [69-71].

Figure 10. (a) Molar carbon yield as a function of time-on-stream for the conversion of xylose to xylitol at 373 K, 2.34 MPa, and WHSV = 5.8 h⁻¹ using the fresh Co/TiO₂ 873C-873R. (b) Molar carbon yield as a function of time-on-stream for the conversion of furfural to furfuryl alcohol at 353 K, 2.34 MPa and WHSV = 17.5 h⁻¹ using the Co/TiO₂ 873C-873R after regeneration. Regeneration of the catalyst was carried out by calcining the catalyst at 873 K and then re-reducing the catalyst at 873 K.

4. Conclusions

The results of this paper show that high-temperature reduction treatments of a Co/TiO₂ catalyst can stabilize the Co/TiO₂ catalyst by SMSI protecting the cobalt particles against leaching and sintering during aqueous-phase reactions. The SMSI effect stabilized the cobalt catalyst in a similar way that ALD stabilizes supported metal catalysts. The SMSI effect enabled the Co/TiO₂ catalyst to selectively cleave C-O-C bond in furan ring, thereby producing 1,5-

pentanediol from furfuryl alcohol. The selectivity toward 1,5-pentanediol was changed by calcination treatments. Moreover, the Co/TiO₂ 873C-873R catalyst had over 95 % yield for hydrogenation of C=O bond to C-OH bond. These results open the door for the practical utilization of inexpensive base-metal catalysts for aqueous-phase conversion of renewable feedstocks and also demonstrate a more practical method to prepare stable supported base-metal catalysts.

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