Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Enhanced Stability of Cobalt Catalysts by Atomic Layer Deposition for Aqueous-Phase Reactions

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Methods

1. Synthesis of non-ALD cobalt catalysts

1.1. Co/γ-Al_2O_3

Gamma-alumina (γ-Al_2O_3, S_{BET} = 142 m^2 g^{-1}, CATALOX® SBa-150 ALUMINA, Sasol North America Inc.) was used as the support. 5 wt% cobalt was deposited on the support by incipient wetness impregnation with aqueous solutions of cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, 98%). After impregnation, the catalyst was dried at 373 K for 12 hours, followed by calcination in flowing air at 573 K (heating rate: 1 K min^{-1}) for 2 hours.

1.2. Co/TiO_2

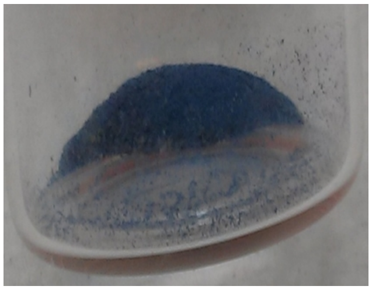
Titania (TiO_2, S_{BET} = 51 m^2 g^{-1}, Aldrich No. 718467) was calcined at 1023 K (heating rate: 4 K min^{-1}) for 4 hours. The calcined TiO_2 (TiO_2-1023) was used as the support. 5 wt% cobalt was deposited on the support by incipient wetness impregnation with aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich, $\geq$ 98%). After impregnation, the catalyst was dried at 373 K for 12 hours, followed by calcination in flowing air at 573 K (heating rate: 1 K min^{-1}) for 2 hours.

2. Synthesis of ALD coated cobalt catalysts

2.1. Al_2O_3/Co/γ-Al_2O_3

ALD Al_2O_3 films were deposited in a fluidized bed reactor described elsewhere.[1] Argon was used as a carrier gas at a flow of 30 sccm, with the reactor pressure varying between 5.3 ± 0.5 Torr during depositions. Trimethyl aluminum (TMA, Sigma-Aldrich, 97%) was held in a cylinder at room temperature and fed through a metering valve to give a partial pressure of ~0.8 Torr. DI water was held in a cooling bath at 285 K. Al_2O_3 depositions were performed at the reactor temperature of 473 K, using 30 cycles consisting of the pulse sequence of TMA – Purge – H_2O – Purge. Purges were fixed at 10 minutes, and pulse lengths were determined by using a quadrupole mass spectrometer monitoring reaction byproducts in the reactor effluent. The Al_2O_3 deposition was performed on 5 g of catalyst (i.e. Co/γ-Al_2O_3) as a substrate. The growth rate of Al_2O_3 overcoat is 1.1 Å/cycle.[2]

We found that after high temperature calcination the color of the calcined Al_2O_3/Co/γ-Al_2O_3 catalyst became blue (see picture below). Blue is the color of cobalt aluminate.[3]



2.2. TiO_2/Co/TiO_2

ALD TiO_2 films were deposited in the same fluidized bed reactor. Argon was used as a carrier gas at a flow of 30 sccm, with the reactor pressure varying between 6.3 ± 0.5 Torr during depositions. Titanium tetrachloride ($TiCl_4$, Acros, 99.9%) was held in a bubbler at 290 K ± 0.1 K. DI water was held in a cooling bath at 285 K. TiO_2 depositions were performed at the reactor temperature of 423 K, using 30 cycles consisting of the pulse sequence of $TiCl_4$ – Purge – H_2O – Purge. Purges were fixed at 10 minutes, and pulse lengths were determined by using a quadrupole mass spectrometer monitoring reaction byproducts in the reactor effluent. A typical deposition used about 1 g of catalyst (i.e. Co/TiO_2) as a substrate.

3. Hydrogen chemisorption

Static H_2 chemisorption was carried out in a Micromeritics ASAP 2020 system. A TiO_2/Co/TiO_2 sample was calcined at 873 K (5 K min^{-1}) in air flow for 2 hours (TiO_2/Co/TiO_2-873) before being loaded in the cell. Before H_2 chemisorption, samples were reduced in situ under H_2 flow at 723 K (heating rate: 1 K min^{-1}) for non-ALD Co/TiO_2 and 873 K (heating rate: 1 K min^{-1}) for TiO_2/Co/TiO_2, held for 2 hours, purged with He for 2 hours, evacuated for 140 minutes, and cooled down to room temperature. Hydrogen was dosed on the catalyst until the equilibrium pressure was 560 mmHg. The hydrogen in the cell was then evacuated at room temperature. After this 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 second isotherm from the first one.

4. BET

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

5. Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) was performed using a Micromeritics AutoChem II 2920 unit. Before a TPR run, samples were pretreated in He at 423 K for 30 minutes. A TPR run was carried out in a flow of 10% H_2/Ar 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 H_2 was monitored using the TCD.

6. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

The liquid samples produced from the reaction were analyzed using a Perkin-Elmer Plasma 400 ICP Emission Spectrometer to quantify leaching of the cobalt catalysts. The samples were prepared by being dissolved in 10% hydrochloric acid. A cobalt (Fluka, 1000 ± 2 mg L^{-1}) was used as standard for ICP.

7. Total Organic Carbon (TOC) Analysis

Total organic carbon (TOC) measurements were performed with a Shimadzu TOC-VCPH Analyzer for the liquid samples produced from the reaction to measure the overall carbon balance. Calibrations were performed with carbon standards supplied by SpectroPure.

8. Transmission Electron Microscopy (TEM)

A Tecnai TF-30 transmission electron microscope operated at 300 keV was used for TEM imaging. The as-deposited and annealed samples were suspended in analytical grade methanol and then collected on a 300 mesh carbon holey support film.

9. Small-Angle X-Ray Scattering (SAXS)

The SAXS experiments were performed at 12-ID-B station with X-ray energy of 12 keV at the Advanced Photon Source of the Argonne National Laboratory. The two-dimensional images were radially averaged to produce 1-D plots of scattered intensity $I(q)$ versus q, where $q = 4\pi (\sin\theta) / \lambda$. θ is scattering angle and λ is wavelength. A Pilatus 2M detector (Dectris Ltd.) was used to acquire scattering data with typical exposure times in a range of 0.1 - 1.0 seconds.

10. High-Resolution X-Ray Diffraction (HRXRD)

HRXRD was performed by synchrotron radiation at Argonne National Laboratory on the Advanced Photon Source (APS), beamline 11-BM using a 12-analyzer Si detector with X-ray energy of 30 keV.

11. Catalyst test in a continuous flow reactor

Aqueous-phase hydrogenation reactions were conducted in a stainless-steel tubular flow reactor (50 cm long, 6.35 mm of outer diameter), heated by a furnace (Lindberg, type 54032). Feedstocks were furfuryl alcohol (Aldrich, 98%), furfural (Sigma-Aldrich, 99%), and xylose (Acros, 99%). Reactants including 2 wt% feed solution and hydrogen gas (Airgas, 99.995%) were flowing upwardly. 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 reaction without catalyst to confirm that there is no homogeneous reaction and no effect of the reactor materials.

For catalytic activity measurements, 0.5 g of the catalyst without diluents was loaded into the reactor with quartz wool packed on both sides. Before the reaction, the non-ALD catalysts were reduced in situ under H_2 flow (100 ml min^{-1}) at 723 K (heating rate: 1 K min^{-1}) and then held for 2 hours. ALD-overcoated catalysts were calcined in situ under air flow (100 ml min^{-1}) at 873 K (heating rate: 5 K min^{-1}) for 2 hours, purging with helium at ambient temperature for 30 minutes, followed by reduction in H_2 flow (100 ml min^{-1}) at 873 K (heating rate: 1 K min^{-1}) for 2 hours. For one cycle of regeneration of catalyst, the catalyst after a reaction was re-calcined at 873 K (heating rate: 2 K min^{-1}) in air flow (100 ml min^{-1}) for 2 hours, purging with helium at ambient temperature for 30 minutes, followed by re-reduction at 873 K (heating rate: 1 K min^{-1}) in H_2 flow (100 ml 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% feed solution was then co-fed to the reactor with hydrogen (40 ml min^{-1}) using a Varian HPLC pump. A stainless-steel gas–liquid separator (150 ml) was used to accumulate liquid products at the top of the reactor. The gaseous products continued to flow to the back-pressure regulator to maintain the reaction pressure. Both an excess flow shut-off valve (Parker Hannifin Corporation, FS190) and a pressure relief valve (Swagelok®, SS-4R3A) were also installed in the reactor system to ensure safe operation. An online GC (Shimadzu GC-2014) was used to analyze the reactor effluent gas. Gaseous products were analyzed using a flame ionization detector (FID) with Rt®-Q-Bond (Restek, Catalog No. 19744) capillary column and a TCD with a GS-Carbon PLOT (Agilent, Catalog No. 113-3133) capillary column. The liquid product 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 aqueous phase products were analyzed using an offline GC-FID (Shimadzu GC-2010) with Rtx®-VMS (Restek, Catalog No. 19915) capillary column and HPLC (Shimadzu LC-20AT) with UV-Vis (SPD-20AV) and RID

(RID-10A) detectors. Based on TOC analysis of liquid samples and GC analysis of gaseous products the carbon balance was between 91 and 95% for each reaction performed.

Table S1. H_2 uptake, reducibility, and BET surface area of TiO_2, Co/TiO_2, and $TiO_2/Co/TiO_2$.

Material	H_2 uptake[(a)] (μmol g^{-1})	Reducibility[(b)] (%)	BET Surface area (m^2 g^{-1})	Pore volume[(c)] (cm^3 g^{-1})
TiO_2	-	-	51.4	-
TiO_2-1023	-	-	10.2	-
Co/TiO_2	7.38	41.7[(d)]	10.1	-
$TiO_2/Co/TiO_2$	0.73	-	9.9	-
$TiO_2/Co/TiO_2$-873	2.01	38.4[(e)]	10.6	0.065
$TiO_2/Co/TiO_2$-used[(f)]	2.79	-	8.6	0.080

[(a)] H_2 uptake determined by static H_2 chemisorption

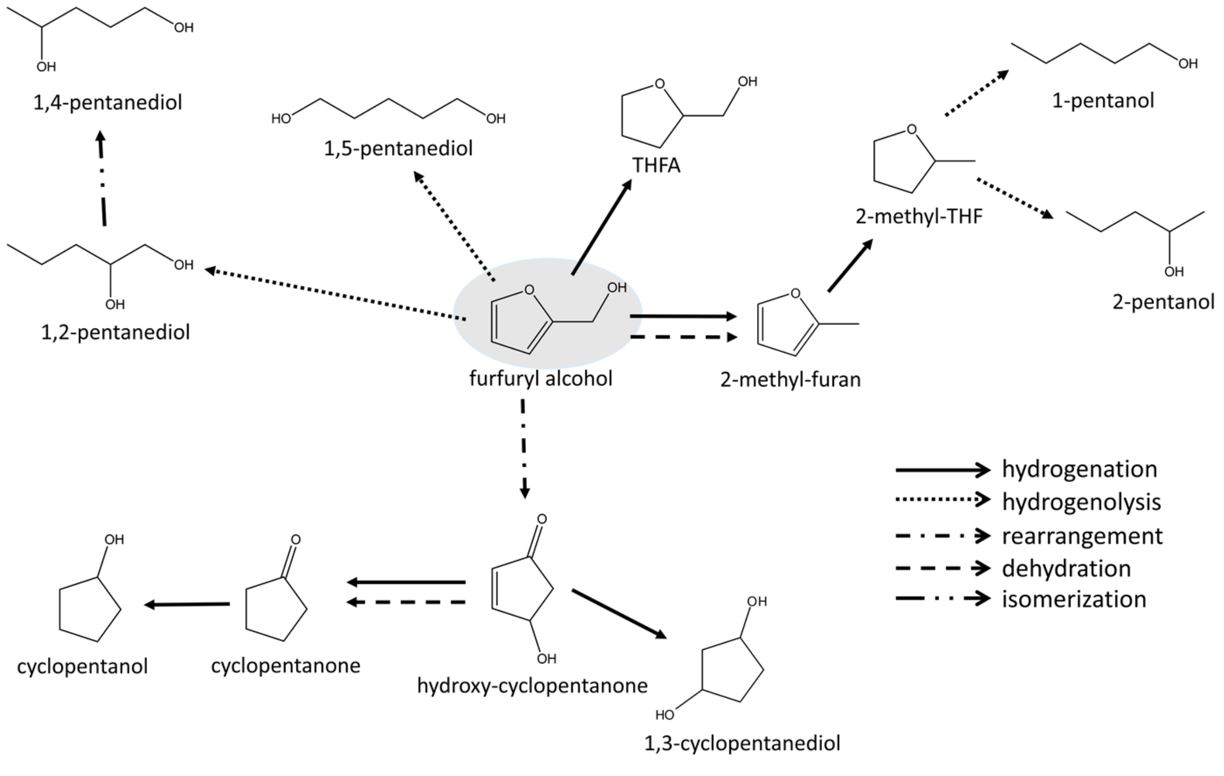
[(b)] Reducibility calculated from areas of H_2-TPR patterns

[(c)] Pore volume measured by N_2 adsorption-desorption isotherm

[(d)] measured at 473~773 K

[(e)] measured at 723~998 K

[(f)] the used $TiO_2/Co/TiO_2$ (after calcination, three reactions, and two regenerations) calcined at 873 K, reduced at 873 K, and then passivated



Scheme S1. Proposed reaction pathways for APH of furfuryl alcohol over $TiO_2/Co/TiO_2$.

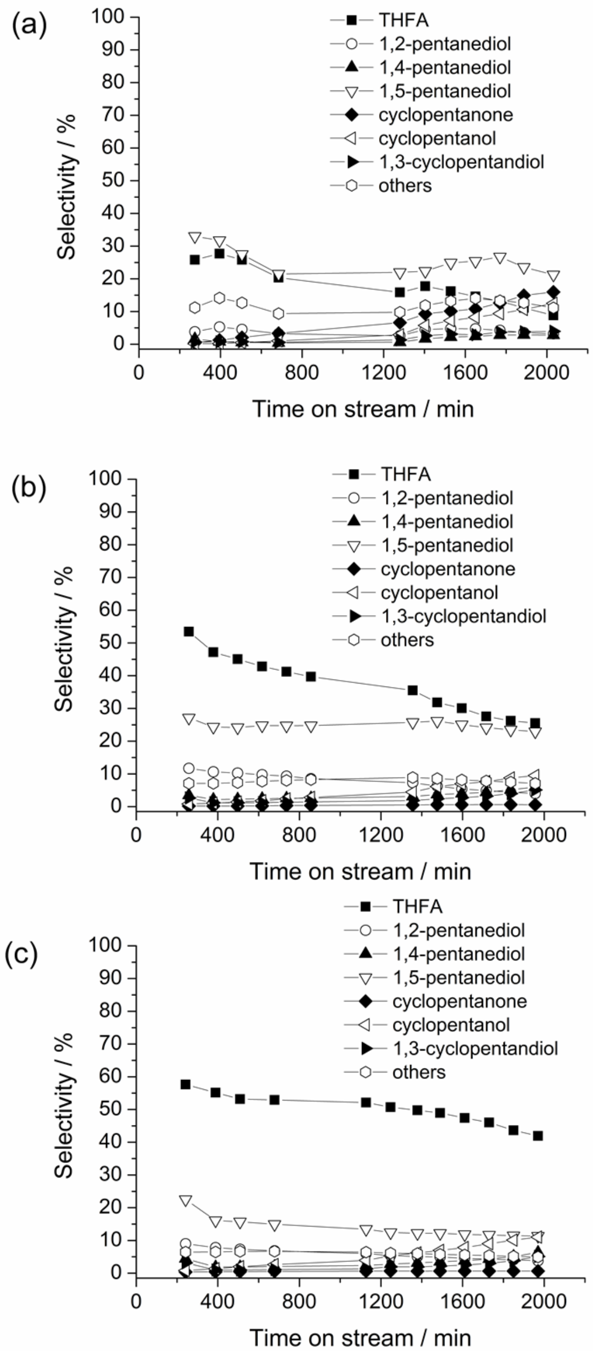


Figure S1. Carbon molar selectivity as a function of time on stream for APH of furfuryl alcohol over (a) $TiO_2/Co/TiO_2$ – fresh, (b) $TiO_2/Co/TiO_2$ – regenerated × 1, and (c) $TiO_2/Co/TiO_2$ – regenerated × 2. Others include 1-propanol, 1-butanol, tetrahydrofuran (THF), 2-methyl-furan, 2-methyl-THF, 1-pentanol, and 2-pentanol. Reaction conditions: 413 K, 2.34 MPa, WHSV = 5.8 h^{-1}, 2 wt% furfuryl alcohol solution as the feed, and H_2 flow of 40 ml min^{-1}.

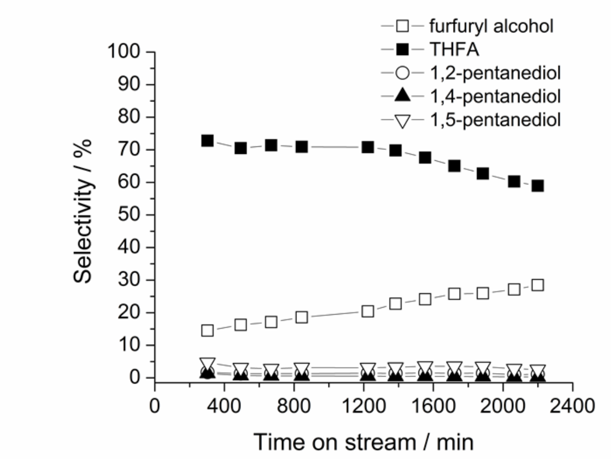


Figure S2. Carbon molar selectivity as a function of time on stream for APH of furfural over $TiO_2/Co/TiO_2$ (after three regenerations) at 100% conversion. Reaction conditions: 373 K, 2.34 MPa, WHSV = 2.2 h^{-1}, 2 wt% furfural solution as the feed, and H_2 flow of 40 ml min^{-1}.

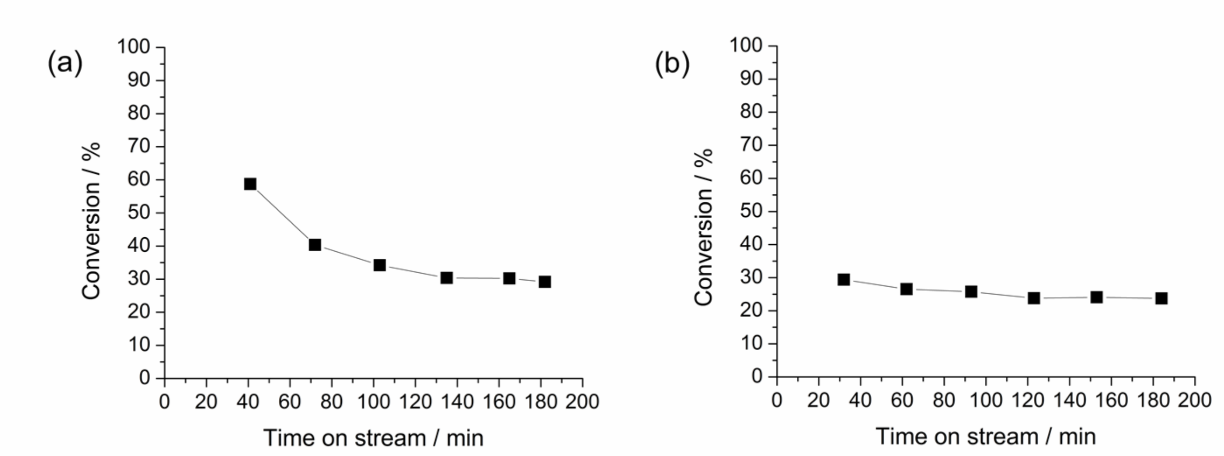


Figure S3. Conversion as a function of time on stream (a) for APH of furfural (furfuryl alcohol was only product) over $TiO_2/Co/TiO_2$ (after four regenerations) and (b) for APH of xylose (xylitol was only product) over $TiO_2/Co/TiO_2$ (after five regenerations). Reaction conditions: 373 K, 2.34 MPa, WHSV = 92.1 h^{-1}, 2 wt% furfural solution as the feed, and H_2 flow of 40 ml min^{-1}.

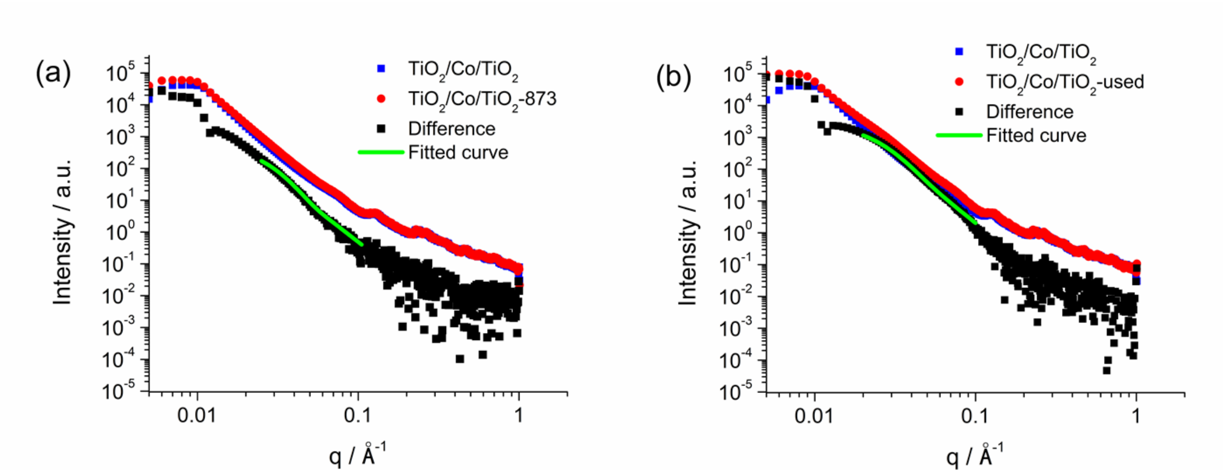


Figure S4. (a) SAXS data of TiO_2/Co/TiO_2 before (blue curve) and after calcination at 873 K (red curve). (b) SAXS data of TiO_2/Co/TiO_2 before calcination (blue curve) and the used TiO_2/Co/TiO_2 (after calcination, three reactions, and two regenerations) calcined at 873 K, reduced at 873 K, and then passivated (red curve). The difference (black curve) subtracts blue curve from red curve.

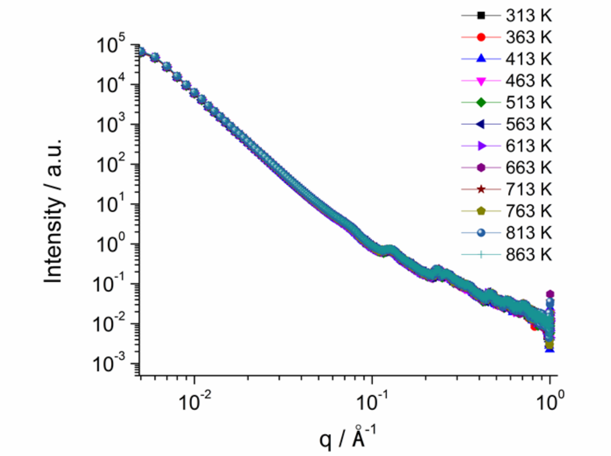


Figure S5. In situ SAXS data of TiO_2-1023.

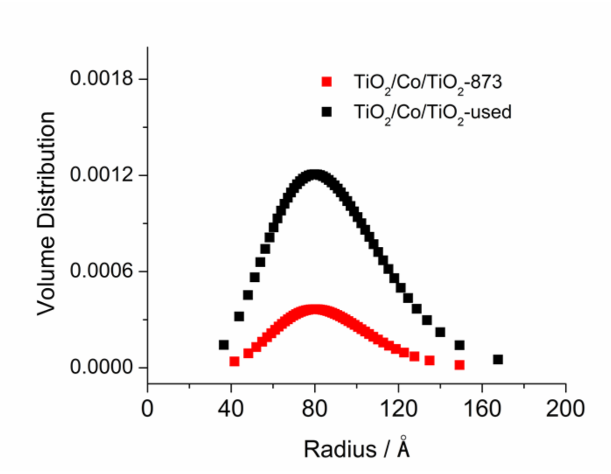


Figure S6. Pore size distribution of $TiO_2/Co/TiO_2$ calcined at 873 K and the used $TiO_2/Co/TiO_2$ (after calcination, three reactions, and two regenerations) calcined at 873 K, reduced at 873 K, and then passivated.

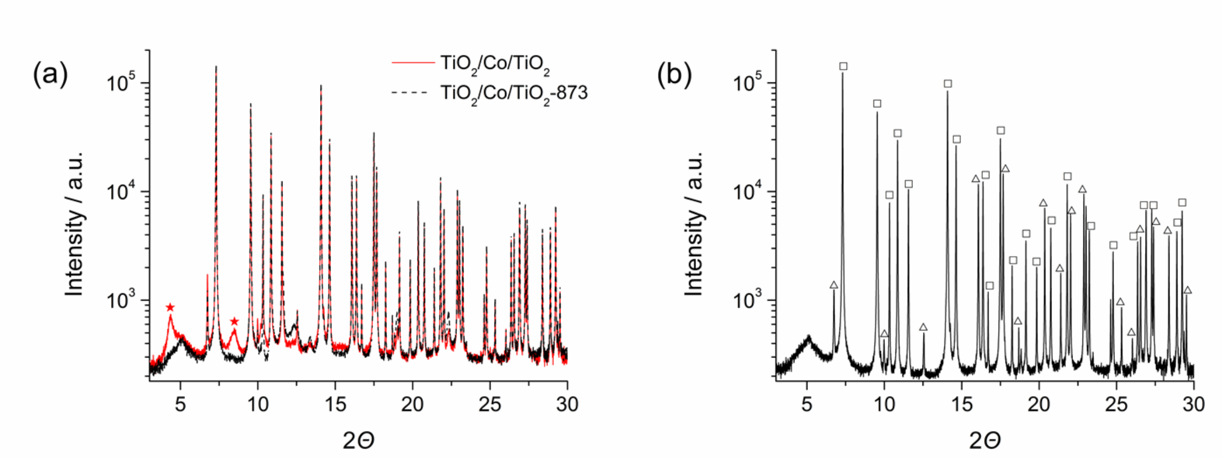


Figure S7. (a) XRD pattern of $TiO_2/Co/TiO_2$ before and after calcination at 873 K (no cobalt and cobalt oxide peak present). (b) XRD pattern of TiO_2 calcined at 1023 K (△ and □ represent anatase and rutile, respectively).

References:

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2. A. W. Ott, J. W. Klaus, J. M. Johnson and S. M. George, *Thin Solid Films*, 1997, **292**, 135-144.
3. P. H. Bolt, F. Habraken and J. W. Geus, *J. Solid State Chem.*, 1998, **135**, 59-69.