

Enhanced Ammonia-Borane Decomposition by synergistic catalysis using CoPd nanoparticles supported on titano-silicates

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Experimental Section

Catalyst Preparation

Synthesis SiO_2 and $\text{Ti}_{0.01}\text{-SiO}_2$. The mesoporous silica has been prepared adapting a synthetic protocol described elsewhere [1,2]. For the synthesis, 0.400 g of surfactant (Pluronic F127), 0.452 g of urea, and 5.052 g of aqueous acetic acid (0.01 M) were mixed under vigorous stirring for 80 min, the final pH of the solution being around 4. Then the solution was cooled in an ice–water bath maintaining the stirring and the silica precursor was added dropwise (2.030 g TMOS). This solution was kept under stirring for 40 min at 0 °C. The sol was introduced in a teflon autoclave. Then, the autoclave was heated at 40 °C for 20 h to produce the aging of the sol (the pH after this step was around 4) followed by a hydrothermal treatment at 120 °C for 6 h, to produce the urea decomposition (the final pH of the supernatant liquid was around 9–10). The final product was then calcined at 550 °C for 6 h (heating rate 3°C/min).

For the well dispersed metal Ti into silica framework ($\text{Ti}_{0.01}\text{-SiO}_2$) the necessary amount of Ti precursor (titanium(IV) ethoxide, Sigma-Aldrich) was added dropwise to the TMOS solution, and then both precursors were added to the initial surfactant solution (vide supra).

Synthesis of Pd and $\text{Co}_x\text{Pd}_{1-x}$ Nanoparticles. Pd and CoPd nanoparticles were prepared by the reduction by solvent modifying the procedure described in other works of our research group

[1,3]. For the synthesis of the nanoparticles, palladium and cobalt precursors were palladium acetate ($\text{Pd}(\text{OAc})_2$, 98%, Sigma-Aldrich) and cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich). The synthetic procedure was carried out in an inert atmosphere using a Schlenk system, according to the following procedure in bimetallic nanoparticles for a total metal amount of 1 mmol and with a equimolar ratio of Co/Pd. Solution 1; 1.114 g of polyvinylpyrrolidone (PVP 30K, Sigma- Aldrich), used as capping agent (PVP/M ratio 10) and the cobalt precursor were added to 60 ml of ethylene glycol in a three-necked round-bottomed flask and the solution was stirred at 80 °C for 2 h using a magnetic stirrer. The resulting solution was of pink color. Solution 2; 0.0562 g of $\text{Pd}(\text{OAc})_2$ were dissolved in 25 ml of dioxane by stirring for 2 h at room temperature using a magnetic stirrer. The color of this solution was light orange.

Solution 1 was then cooled down to 0 °C in an ice bath and the necessary amount of aqueous 1 M NaOH solution was added under stirring in order to adjust the pH of the solution to 10. Then, solution 2 was poured into solution 1 under vigorous stirring in order to ensure homogenization and the final mixture was heated up to 100 °C. The solution changed its color from light orange to dark brown, which indicated that the metallic colloid had been formed. Then, heating was maintained for 2 h, after which the bath was removed and the colloidal suspension was cooled down to room temperature.

The prepared bimetallic nanoparticles were purified and redispersed in methanol. The purification was carried out by pouring the colloid into a glass bottle, adding an excess of acetone and leaving the mixture overnight. The supernatant organic phase was removed and

the purified nanoparticles were redispersed by swirling in a known amount of methanol, so that the final suspension concentration was perfectly known. In case of pure Pd nanoparticles, the cobalt precursor was not added to solution 1 in the synthesis and the palladium precursor amount was readjusted. In this work, pure Pd nanoparticles and 3 samples with different nominal CoPd molar ratios ($\text{Co}_{0.25}\text{Pd}_{0.75}$, $\text{Co}_{0.5}\text{Pd}_{0.5}$ and $\text{Co}_{0.75}\text{Pd}_{0.25}$) were prepared.

Nanoparticles Impregnation. The aforementioned silica and silica-based support (SiO_2 and $\text{Ti}_{0.01}\text{-SiO}_2$, respectively) were impregnated by the excess volume impregnation method using the colloidal nanoparticles suspension (pure Pd and CoPd) in methanol for 2 days under magnetic agitation. Then, methanol was removed keeping on the stirring while heating at 65 °C. The samples were prepared with a nominal total metal loading of 1 wt. %.

Catalysts Characterization. The mesoporous silica catalysts support was characterized by N_2 adsorption–desorption at -196 °C and by CO_2 adsorption at 0 °C (Quantachrome, Autosorb 6B) to analyze the porous texture of the materials. Apparent surface area values were calculated from N_2 adsorption isotherms using the BET equation (S_{BET}). Total micropore volume ($V_{\text{DR}}(\text{N}_2)$) and narrow micropore volume ($V_{\text{DR}}(\text{CO}_2)$) were calculated applying the Dubinin–Radushkevich (DR) equation to the N_2 adsorption data at -196 °C and the CO_2 adsorption data at 0 °C, respectively.

The Pd and CoPd loadings in the catalysts were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), in a Perkin-Elmer Optima 4300 system. The extraction of the metal was made by treating the samples with aqua regia at room temperature and adjusting the Pd and Co concentration between 0 and 20 ppm for the analyses. The samples were also characterized by Transmission Electron Microscopy (TEM) with a JEOL JEM-2010 microscope operating at 200 kV with a space resolution of 0.24 nm. For the analysis, a small amount of sample was suspended in a few drops of hexane, and sonicated for few minutes. A drop of this suspension was then deposited onto a 300 mesh Lacey copper grid and left to dry at room temperature. TEM analyses allowed the determination of the average metal particle size.

CO adsorption experiments for the TiSiO₂-based as-prepared catalysts were performed in an automatic device; BEL-CAT (BEL JAPAN, INC) where 30 mg of catalyst were added in a quartz tube reactor. Before the analysis the catalysts were reduced with H₂ at 150 °C to ensure the total reduction of the NPs.

The electronic states were determined by X-ray Photoelectron Spectroscopy (XPS) using a K-Alpha spectrometer from Thermo-Scientific, equipped with an Al anode. Characterization of the electronic states of each element was made from the relative area of the peaks resulting in the 3d, 3p, 2p and 2p region of Pd, Co and Ti, respectively.

The crystalline structure of the obtained supports was analyzed by X-ray Diffraction (XRD) using a Bruker D8-Advance equipment scanning in the 4-80 2θ range with a scan rate of 2°/min.

It must be noted that neither of the supports showed any significant diffraction peaks, which confirmed the amorphous nature of both solids.

The prepared materials were analyzed using a UltraViolet-Visible (UV-Vis, UV-2600, SHIMADZU) equipped with a double monochromator, a photomultiplier tube detector and an integrating sphere which enables the possibility to measure the diffuse reflectance or diffuse transmittance of a solid powder.

Ammonia-Borane Decomposition Tests. The catalysts were analyzed in AB decomposition in two different conditions; dark and under UV-Vis radiation. The reactions were carried out in a Pyrex reaction vessel in case of dark condition reaction (30 ml) sealed with a rubber septum with magnetic agitation, while in the catalytic reactions under UV-Vis conditions the reaction vessel used was made of quartz. In this last case a fan was aimed at the vessel to maintain the temperature and avoid heating of the reactor. For the catalytic tests 10 mg of catalyst and 5 ml of water were introduced in the vessel (in the most active samples, specified in the results section, it was necessary to reduce the amount of catalyst to obtain a representative TOF value). In order to disperse the catalyst and obtain an inert atmosphere the powder was treated in an ultrasound bath for 15 min and bubbled with argon gas for 30 min, respectively. 0.1 ml of AB solution (0.5 M, metal/AB molar ratio of 0.02) was added into the reactor vessel and it was placed in an oil bath at 30 °C with magnetic stirring. The H₂ generated was measured every 2.5 min using a Shimadzu GC14B equipped with an MS5 A column (H₂). For this purpose,

upon injection into the GC the resulting H₂ peak areas were converted into H₂ concentration by using a calibration with the corresponding standard gas.

Results

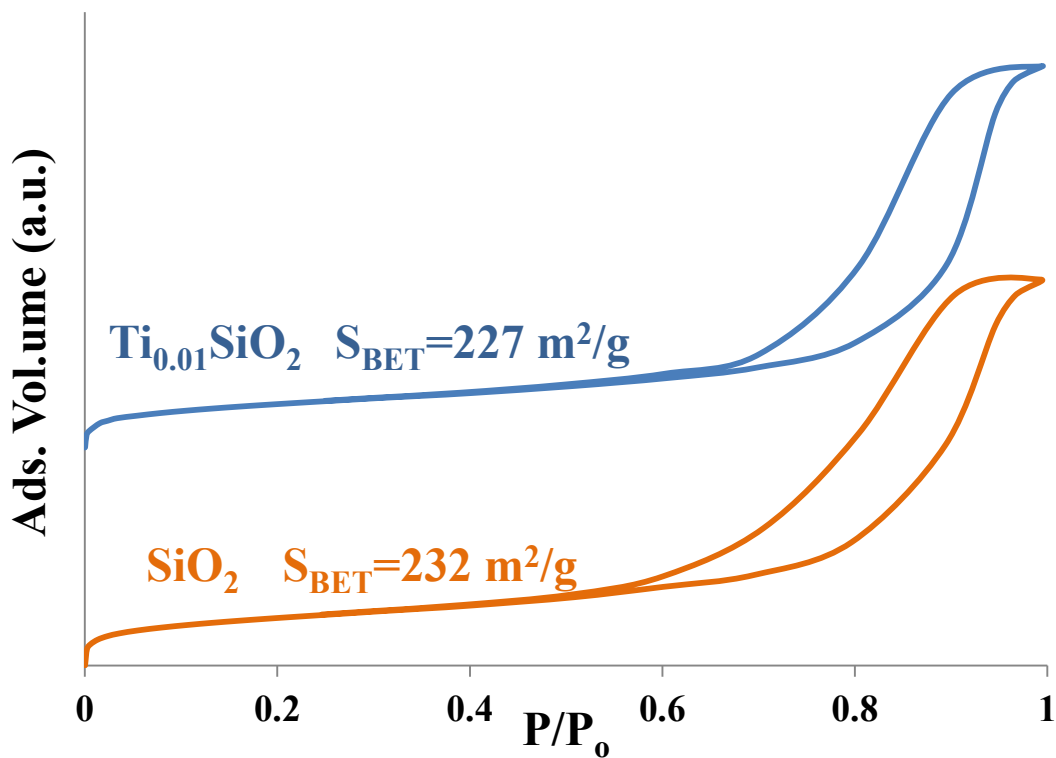


Fig S1. N₂ adsorption isotherms for the raw SiO₂ and Ti-SiO₂ used as support for the Co_xPd_{1-x} NPs. Note: The Ti-SiO₂ isotherm has been shifted up in the y-axis for the sake of visibility.

Table S1. ICP-OES and XPS results from the NPs characterization once they were deposited on the supports.

	Metal loading (wt. %) ^a	Molar Ratio Co/Pd		Pd 3d(5/2) ^b		Ti 2p (3/2) ^b
		ICP ^a	XPS ^b	Pd(0) % (BE (eV))	Pd(II) % (BE (eV))	Ti(IV) BE (eV)
Pd/SiO ₂	1.09	0/1	0/1	73.7 (335.27)	26.3 (337.02)	-
Co _{0.25} Pd _{0.75} /SiO ₂	0.97	0.20/0.80	*	86.0 (335.22)	14.0 (336.56)	-
Co _{0.5} Pd _{0.5} /SiO ₂	0.99	0.46/0.54	0.48/0.52	83.5 (335.13)	16.5 (336.66)	-
Co _{0.75} Pd _{0.25} /SiO ₂	1.02	0.72/0.28	0.68/0.32	69.6 (335.19)	30.4 (336.76)	-
Ti-SiO ₂	-	-	-	-	-	460.48
Pd/Ti-SiO ₂	1.05	0/1	0/1	70.1 (335.57)	29.9 (337.63)	459.38
Co _{0.25} Pd _{0.75} /Ti-SiO ₂	0.99	0.20/0.80	*	78.0 (335.28)	22.0 (336.84)	458.93
Co _{0.5} Pd _{0.5} /Ti-SiO ₂	1.01	0.46/0.54	0.48/0.52	70.3 (335.32)	29.7 (337.06)	458.98
Co _{0.75} Pd _{0.25} /Ti-SiO ₂	1.00	0.72/0.28	0.68/0.32	68.6 (335.47)	31.4 (337.14)	459.25

^a Results calculated from ICP-OES analysis.

^b Binding Energies (BE), Co and Pd content and Pd percentage determined by XPS analysis of their corresponding peaks.

* Due to the low amount of Co content in these samples, the Co signal is very low and the obtained result has not the necessary accuracy to give a reliable result.

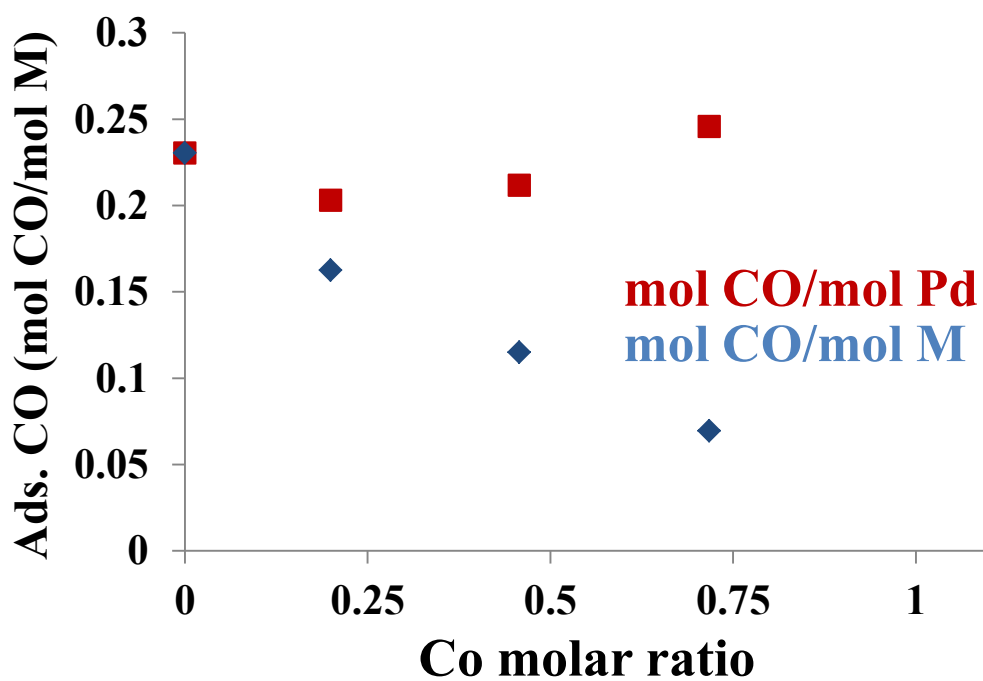


Fig S2. CO adsorption results of the different $\text{Co}_x\text{Pd}_{1-x}\text{-Ti-SiO}_2$ (as representative for all the catalysts) prepared in this work. Red, normalized per Pd mol and blue, normalized per the total metal amount (Co and Pd).

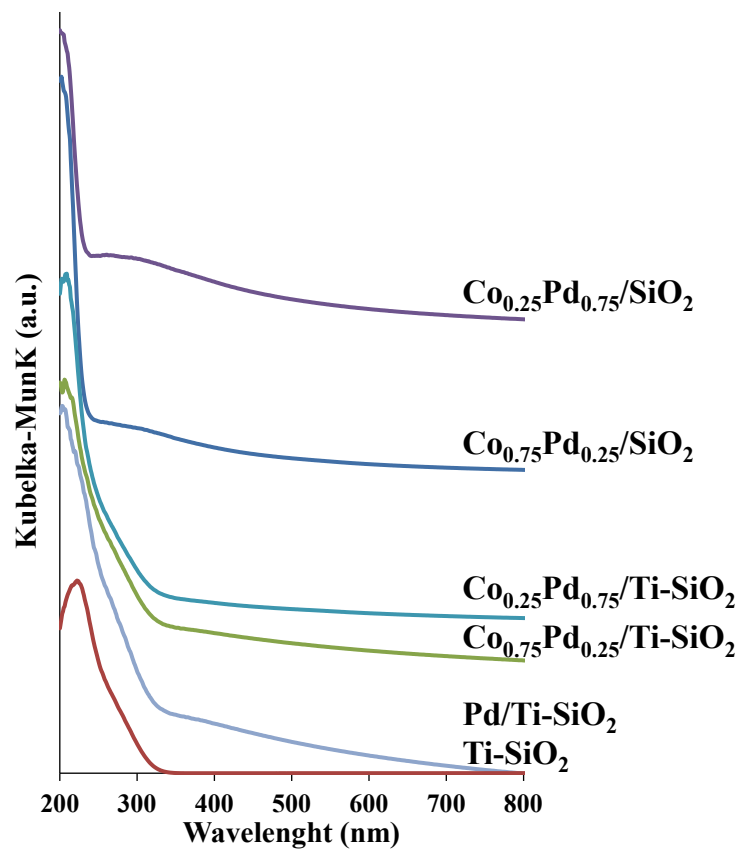


Fig S3. Solid reflectance UV-Vis analysis of the catalysts and supports.

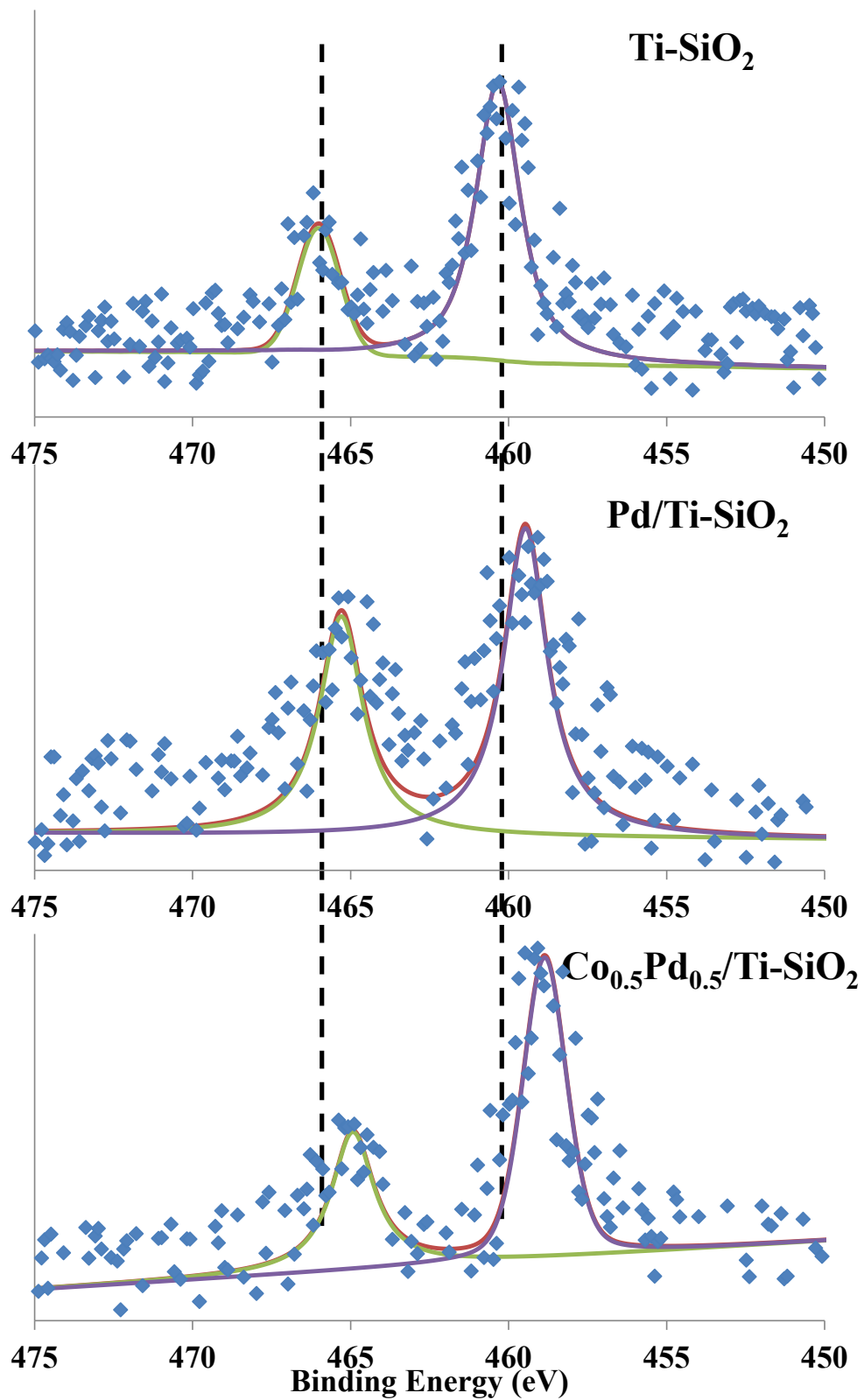


Fig S4. Ti XPS spectra of the raw Ti-SiO_2 support and after deposition of Pd and $\text{Co}_{0.5}\text{Pd}_{0.5}$ NPs.

Dark Conditions
UV-Vis Conditions

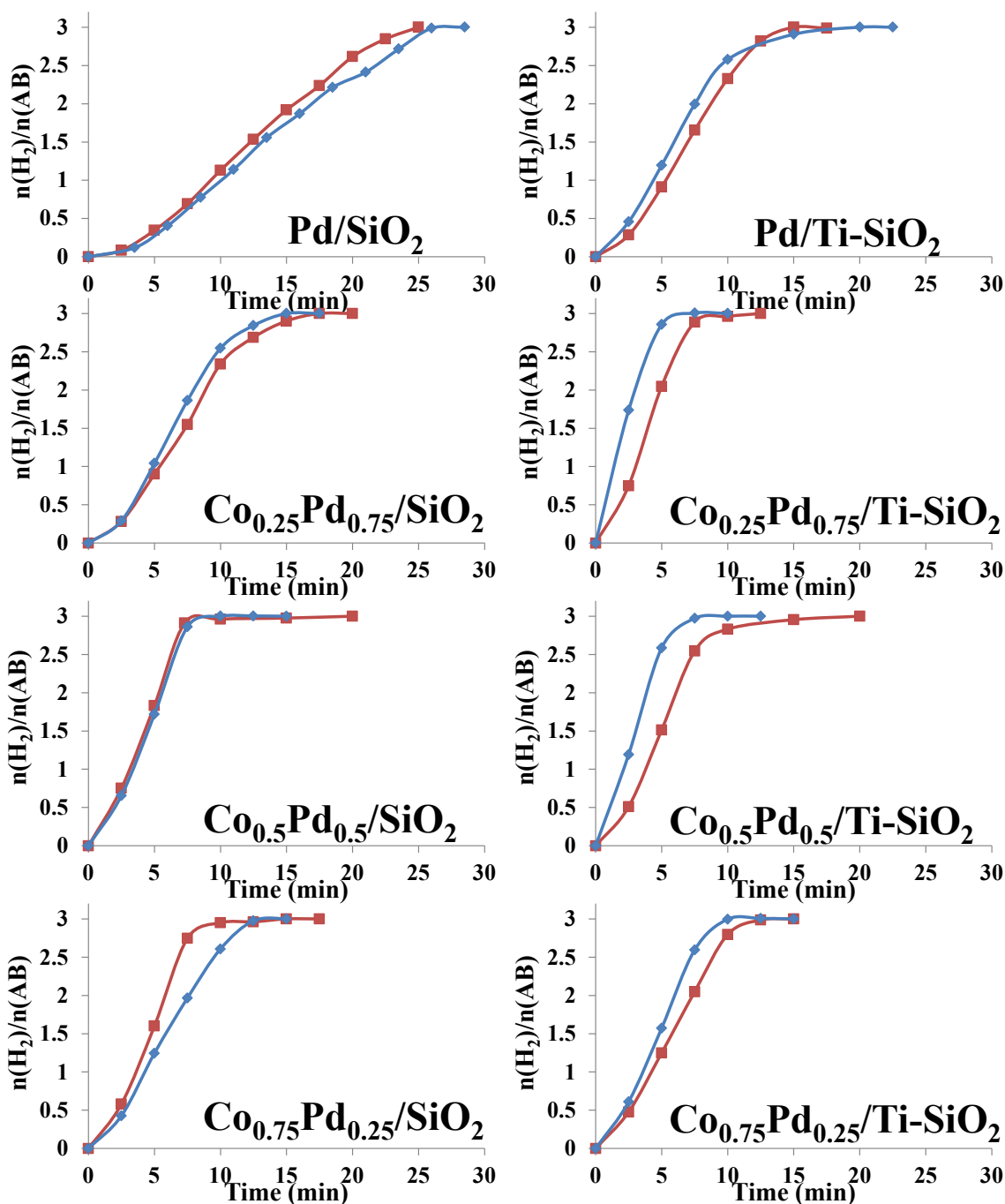


Fig S5. Catalytic conversion of ammonia-borane under dark and UV-Vis irradiation conditions

$(n(\text{H}_2)/n(\text{AB}))$ vs time of all the catalysts.

References

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