Amine Grafted Silica Supported CrAuPd Alloy Nanoparticles: A Superb Heterogeneous Catalyst for the Room Temperature Dehydrogenation of Formic Acid

(Supporting Information)

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(References cited here are independent of the main manuscript)

S.1 Materials

Palladium(II) nitrate dihydrate ($Pd(NO_3)_2.2H_2O$) (~ 40 % Pd basis), chromium(II) nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$), gold(III) chloride trihydrate nitrate ($AuCI_3.3H_2O$), aminopropyltriethoxysilane (APTS; $H_2N(CH_2)_3Si(OC_2H_5)_3$), sodium borohydride ($NaBH_4$), ninhydrin ($C_9H_6O_4$), toluene ($C_7H_8$) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich®. Formic acid (CH_2O_2), and silica gel (230-400 mesh) were purchased from Merck®. Toluene was distilled over sodium and stored in a Labsconco nitrogen-atmosphere drybox (O_2< 1ppm). Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware and Teflon-coated magnetic stir bars were washed with acetone and copiously rinsed with distilled water before drying in an oven at 423 K.

S.2 Characterization

Cr, Au and Pd contents of the samples were determined by ICP-OES (Leeman, Direct Reading Echelle) after each sample was completely dissolved in a mixture of HNO_3/HCl (1/3 v/v). Powder X-ray diffraction (XRD) patterns were recorded with a MAC Science MXP 3TZ diffractometer using Cu-Kα radiation (wavelength 1.54 Å, 40 kV, 55 mA). CTEM, HRTEM, STEM, and HAADF-STEM samples were prepared by dropping one drop of dilute suspension on copper coated carbon TEM grid and the solvent was then dried. The conventional TEM was carried out on a JEOL JEM-200CX transmission electron microscopes operating at 120 kV. HRTEM, STEM and HAADF-STEM were run on a JEOL JEM-2010F transmission electron microscope operating at 200 kV. Oxford EDXS system and Inca software were used to collect and process STEM-EDX data. The XPS analyses were performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al- Kα radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W, and pass energy of 23.5 eV). The gas generated from the decom-position of formic acid was analyzed by FID-2014 and TCD-2014GC analyzers (Shimadzu). UV−Vis electronic absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. FTIR spectra of the samples were taken from a Shimadzu IR Affinity by using modulated gas chambers.

S.3 Preparation of Amine Functionalized Silica (N-SiO_2)

The functionalization of the silica was carried out by adding a desired amount of APTS to 30 mL of dry toluene containing 500 mg of silica. The resulting slurry was allowed to stir for 12 h. The white solid was filtered and washed repeatedly with toluene. The white amine-functionalized silica (N-SiO_2) was dried in a vacuum oven (100 ºC and 10^{-1} Torr) and used for further application. The presence of NH_2 groups on SiO_2 was confirmed by ATR-IR and quantified by the colorimetric ninhydrin method.[1]

S.4 Preparation of CrAuPd/N-SiO_2 (Cr:Au:Pd = 0.15:0.25:0.60) Catalyst

CrAuPd/N-SiO_2 catalyst was simply and reproducibly prepared through the conventional impregnation and subsequent reduction method.[2] Typically, 5.0 mL aqueous solution containing $Pd(NO_3).2H_2O$ (7.13 mg, 26.7 µmol Pd), $Cr(NO_3)_3.9H_2O$ (2.68 mg, 6.7 µmol Cr), $AuCI_3.3H_2O$ (4.37 mg, 11.0 µmol Au) and N-SiO_2 (100 mg, 98 µmol NH_2) is mixed for 3 hours. Then, the fresh 1.0 mL aqueous solution of $NaBH_4$ (28 mg, 0.7 mmol) was added to this mixture and the resulting solution was stirred for half an hour under air at room temperature. After centrifugation (6000 rpm, 5 min.), copious washing with water (3 x 20 mL), filtration, and drying in oven at 373 K, CrAuPd/N-SiO_2 catalyst was obtained as dark gray powders.

S.5 Activity Measurements

The catalytic activity of CrAuPd/N-SiO_2 in the dehydrogenation of FA was determined by measuring the rate of hydrogen generation. The volume of released gas during the reaction

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[1] I. Taylor, A. G. Howard, *Anal. Chim. Acta* **1993**, 271, 77.

[2] R. J. White, R. Luque, V. L. Budarin, J. H. Clark, D. J. Macquarrie, *Chem. Soc. Rev.* **2009**, 38, 481.

was monitored using the gas burette by water displacement.[3] Before starting the catalytic activity test, a jacketed one necked reaction flask (50.0 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer (Heidolph MR-3004) and thermostated to 298 K by circulating water through its jacket from a constant temperature bath (Lab Companion RW-0525). In a typical experiment, CrAuPd/N-SiO_2 catalyst was weighed and transferred into the reaction flask, and then 9.0 mL H_2O was added into the reaction reaction flask and this mixture was stirred for 15 min. to achieve thermal equilibrium. Next, 0.5 mL aqueous FA solution (75 μL FA in 0.425 mL H_2O) was added into the reaction flask via its septum by using a 1.0 mL gastight syringe and the catalytic reaction was started (t = 0 min) by stirring the mixture at 600 rpm.

S.6 Catalytic Selectivity

The selectivity of CrAuPd/N-SiO_2 catalyst in the decomposition of FA was investigated by GC, FTIR analyses and NaOH-trap experiment. The gas generated over PdAg-MnO_x/SiO_2-NH_2 catalyzed dehydrogenation of aqueous FA solution (10.0 mL of 0.3 M) was collected separately in GC analyzing balloon and FTIR-gas cell, which were then analyzed in GC and FTIR by using pure CO, H_2 and CO_2 as reference gases. NaOH-trap experiments were performed to determine the molar ratio of CO_2 to H_2 in the product mixture generated during the CrAuPd/N-SiO_2 catalyzed decomposition of aqueous FA solution (10 mL of 0.20 M). [4] In these experiments, the trap (10.0 M NaOH solution) was placed between the jacketed reactor and gas burette. The generated gas during the reaction was passed through the NaOH trap where CO_2 was captured (**1**). Next, the volume of the gas generated from the dehydrogenation of FA was monitored and compared to those without the trap experiment. We observed that the volume of the generated gas decreased by a factor of two in the presence of the NaOH

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[3] a) Z. L. Wang, J.M. Yan, Y. Ping, H.L. Wang, W.T. Zheng, Q. Jiang, *Angew. Chem. Int. Ed*. **2013**, 52, 4406; b) Zhang, Ö. Metin, D. Su, S. Sun, *Angew. Chem. Int. Ed.* **2013**, 52, 3681.

[4] X. Gu, Z-H. Lu, H-L. Jiang, T. Akita, Q. Xu, *J. Am. Chem. Soc.* **2011**, 133, 11822.

trap. This result is indicative of the complete adsorption of CO_2 in NaOH solution (**1**) and the presence of equivalent molar amounts of CO_2 and H_2 (1.0:1.0) in the product mixture of the CrAuPd/N-SiO_2 catalyzed additive-free FA dehydrogenation.

$$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3\,(aq) + H_2O(l) \quad (\mathbf{1})$$

S.7 Testing the Recyclability Performance of CrAuPd/N-SiO_2 Catalyst

The recyclability of CrAuPd/N-SiO_2 in the dehydrogenation of FA was determined by a series of experiments started with aqueous FA solution (0.20 M in 10.0 mL H_2O) at 298 K. When the complete conversion is achieved, immediately, another equivalent of FA was added to leading further hydrogen evolution from the reaction mixture. The same procedure was followed up to 5th catalytic recycle.

S.8 Isolability and Reusability Performance of CrAuPd/N-SiO_2 Catalyst

After the first run of catalytic dehydrogenation of aqueous FA solution starting with CrAuPd/N-SiO_2 at 298 K, the catalyst was isolated from reaction solution by centrifugation and washed with excess water, then dried at 373 K. The dried catalyst was weighted and used again in the catalytic dehydrogenation of aqueous FA solution (0.20 M in 10.0 mL H_2O) solution at 298 K. The same procedure was followed up to 5th catalytic reuse.

Table S1. Comparison of the catalytic performance of CrAuPd/N-SiO_2 catalyst with the prior best heterogeneous catalyst systems reported for the dehydrogenation of FA in the absence of any additives at ≤ 298 K (references cited herein are those taken from manuscript).

Catalyst	Temp.(K)	Con. (%)	Activity[a]	Reference
Ag@Pd	293	36	63	[8a]
AgPd	293	10	72	[8a]
Ag@Pd/C	293	44	96	[8a]
Au@Pd/N-rGO	298	89	98	[8b]
CoAuPd/C	298	91	37	[8c]
CoAuPd/r-GO	298	51	45	[8d]
CoAuPd/DNA	298	96	85	[8d]
AuPd	298	28	41	[8e]
AgPd	298	52	150	[8f]
Pd-MnO_x/N-SiO_2	293	80	140	[8g]
CrAuPd/N-SiO_2	298	100	730	this study

[a] *initial* TOF values (TOF = mol H_2 / mol catalyst × time (h)) calculated at ~ 20 % of conversion achieved.

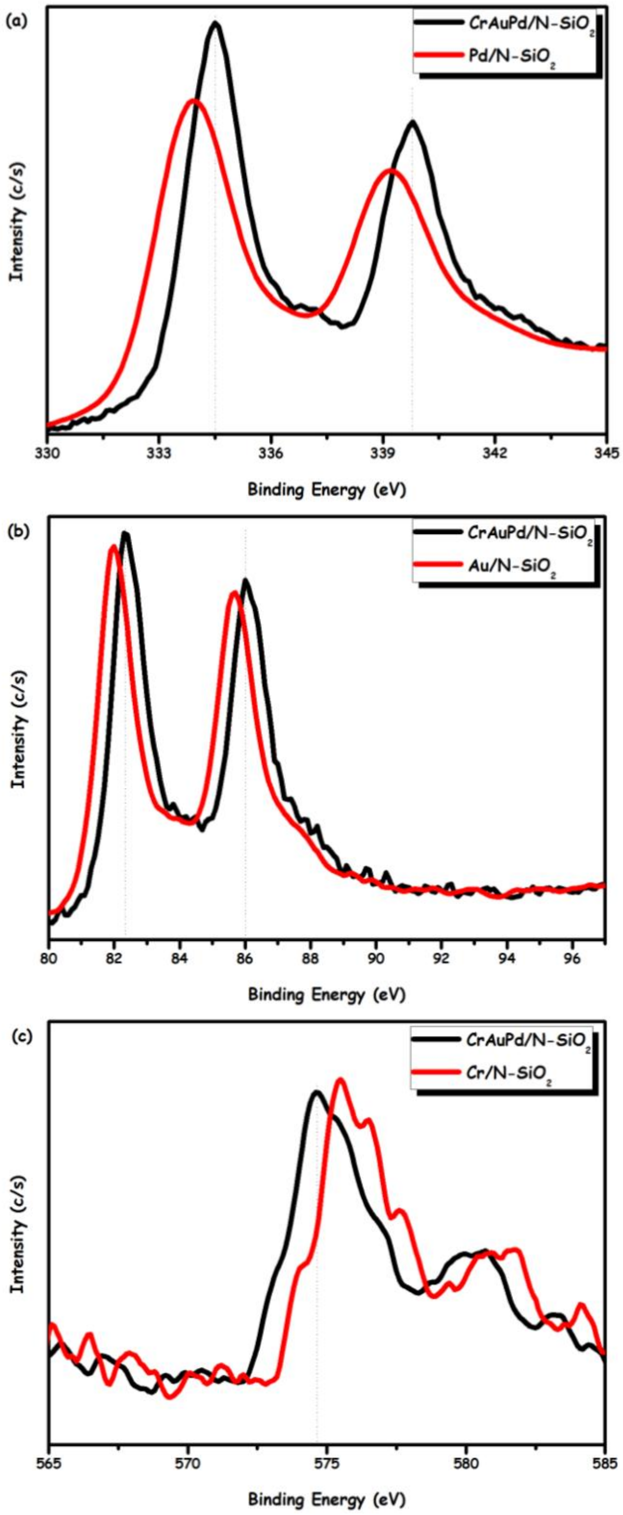

Figure S1. The high resolution (a) Pd 3d XPS spectrum for CrAuPd/N-SiO_2 and Pd/N-SiO_2 (b) Au 4f XPS spectrum for CrAuPd/N-SiO_2 and Pd/N-SiO_2, and (c) Cr 2p XPS spectrum for CrAuPd/N-SiO_2 and Au/N-SiO_2.

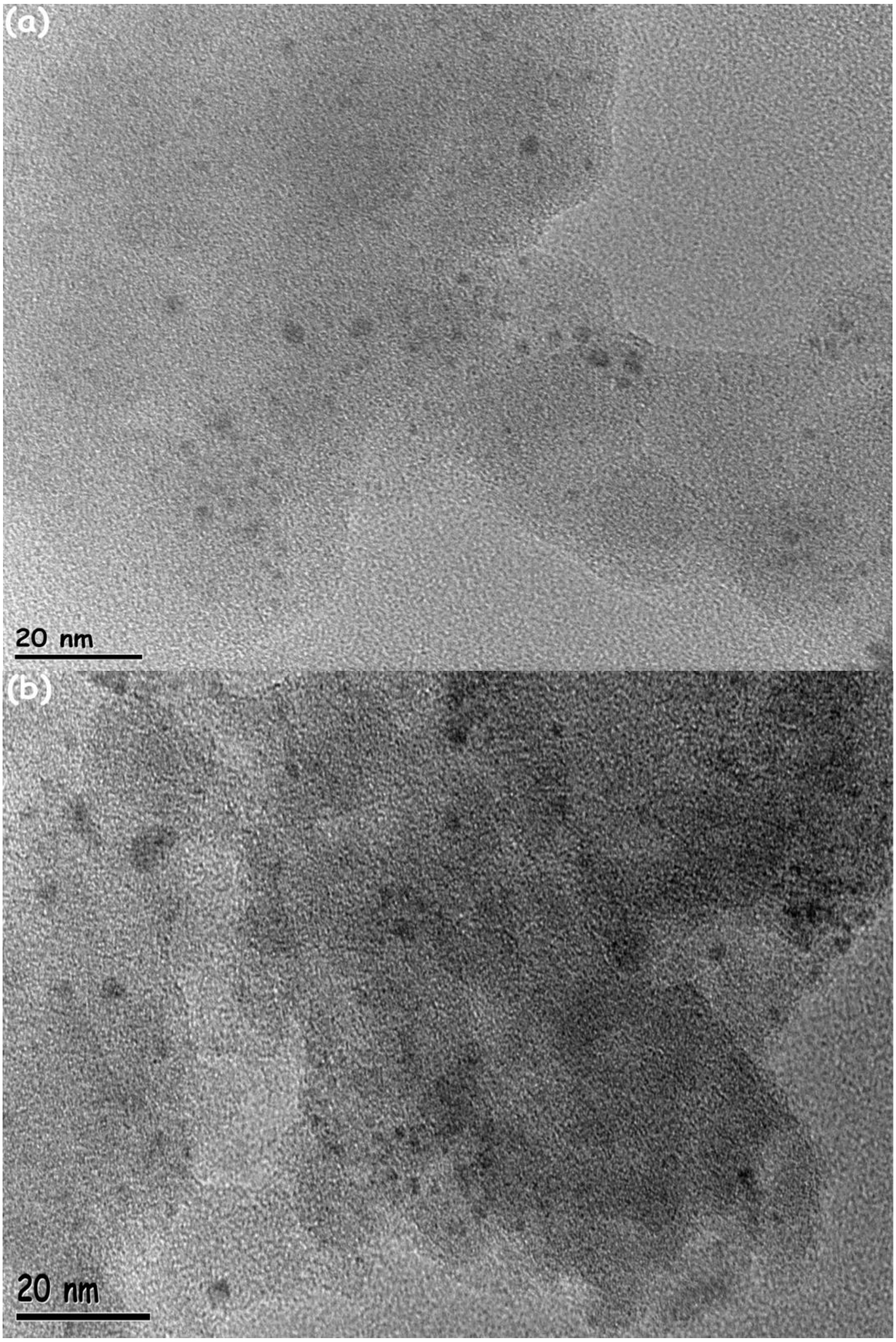

Figure S2. CTEM images of (a) $Pd_{1.0}/N\text{-}SiO_2$ and (b) $Au_{0.45}Pd_{0.55}/N\text{-}SiO_2$ catalysts.

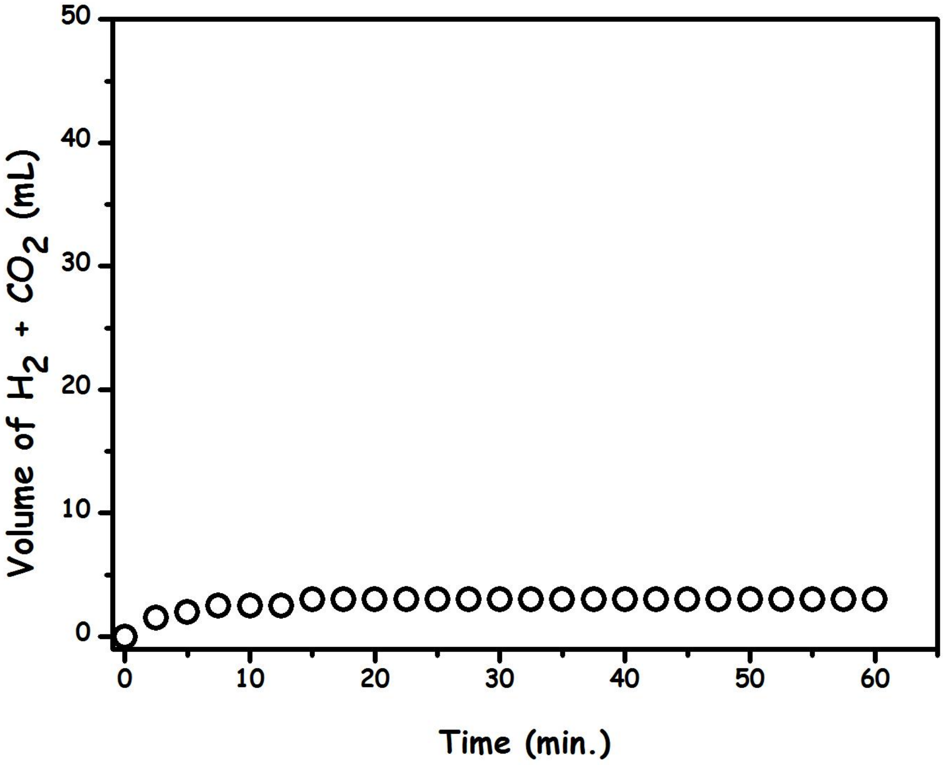

Figure S3. The volume of gas (CO_2 + H_2) (mL) versus time (min.) graph for the dehydrogenation of aqueous FA solution (0.20 M in 10.0 mL H_2O) catalyzed by the phyical mixture of $Cr_{0.17}$/N-SiO_2 $Au_{0.23}$/N-SiO_2 and $Pd_{0.60}$/N-SiO_2 catalysts at 298 K.

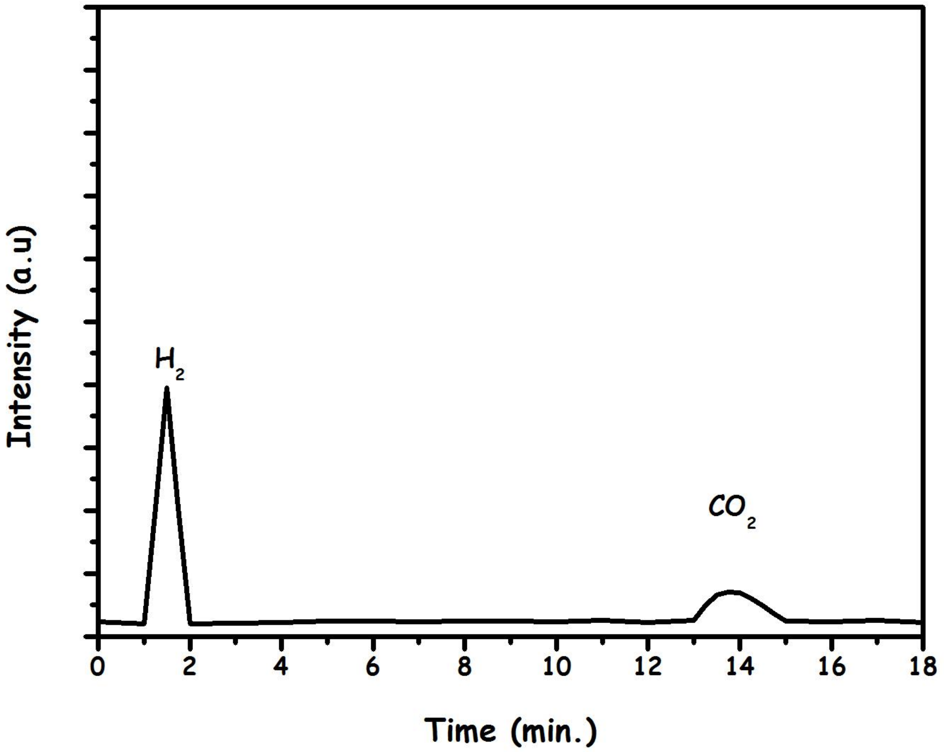

Figure S4. The gas chromatogram (GC/TCD) of the evolved gas from aqueous FA solution (0.20 M in 10.0 mL H_2O) over $Cr_{0.15}Au_{0.25}Pd_{0.60}/N\text{-}SiO_2$ catalyst at 298 K.

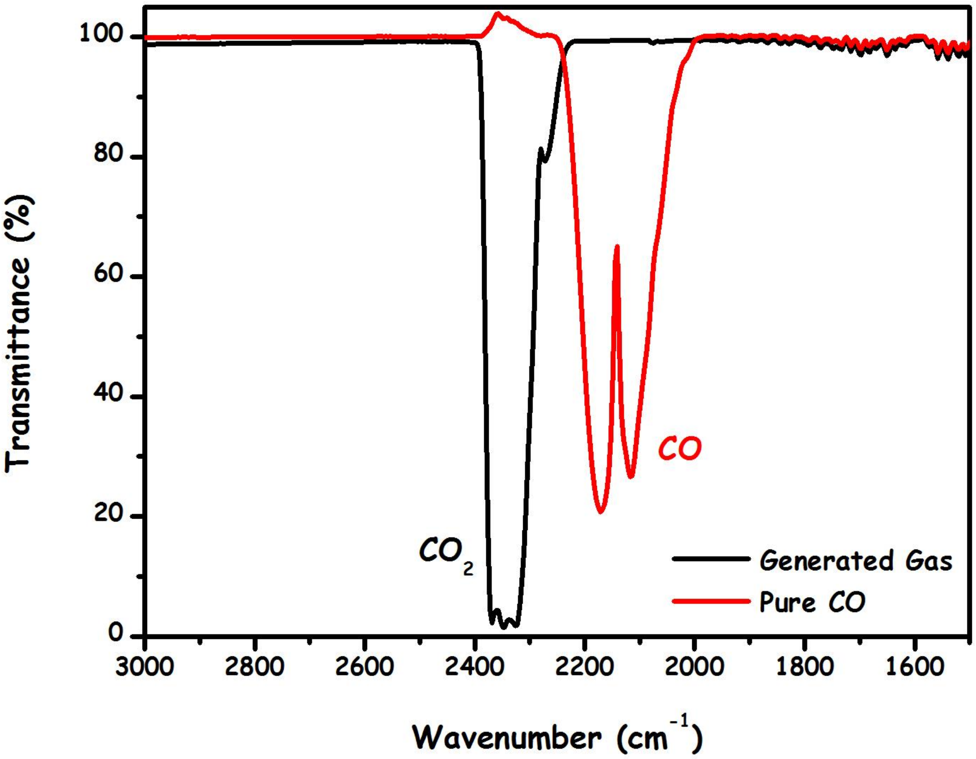

Figure S5. FTIR spectra of the pure CO and generated gas from aqueous FA solution (0.20 M in 10.0 mL H_2O) over $Cr_{0.15}Au_{0.25}Pd_{0.60}$/N-$SiO_2$ catalyst at 298 K.

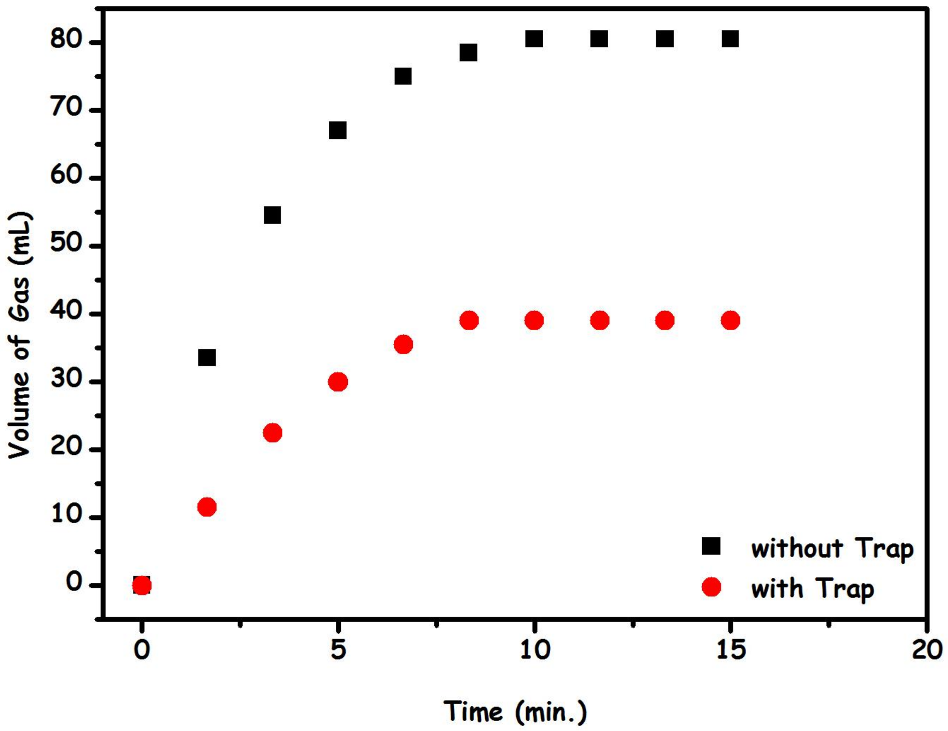

Figure S6. The volume of gas (CO_2 + H_2) (mL) versus time (min.) graph for $Cr_{0.15}Au_{0.25}Pd_{0.60}$/N-$SiO_2$ ([CrAuPd] = 4.0 mM) catalyzed dehydrogenation of aqueous FA solution (0.20 M in 10.0 mL H_2O) in the presence and absence of NaOH trap ([NaOH] = 10.0 M) at 298 K.

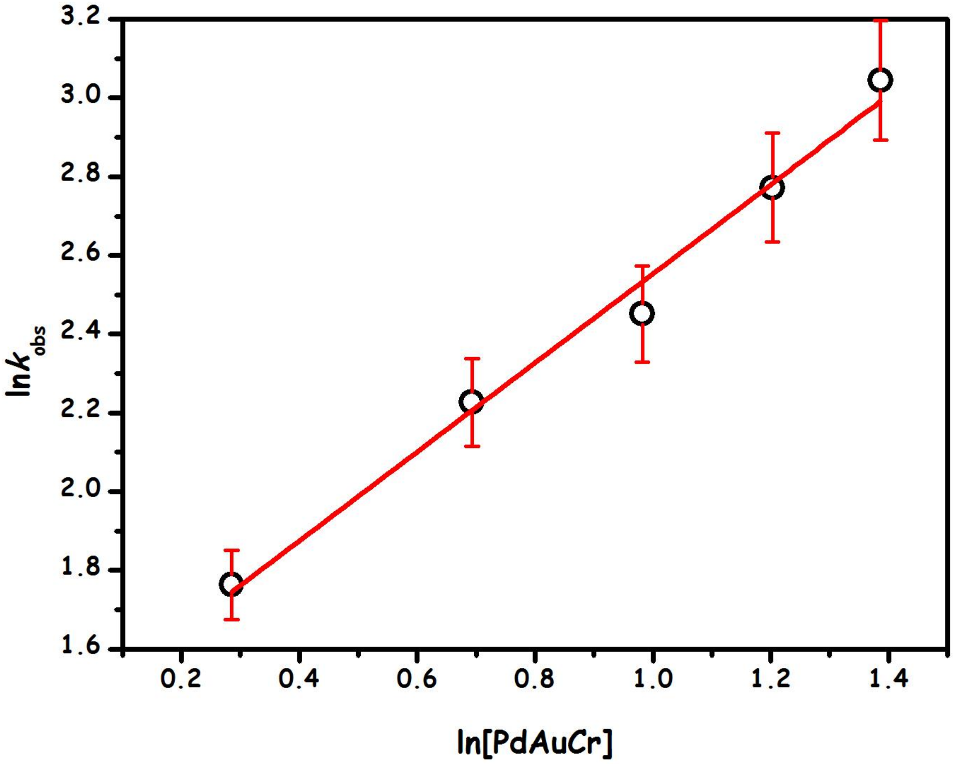

Figure S7. Plot of the observed rate constant (k_{obs}) versus the catalyst concentration (both in logarithmic scale; $y = 0.42 + 1.13x$ and $R^2 = 0.987$) for the dehydrogenation of aqueous FA solution (0.20 M in 10.0 mL H_2O) starting with different $Cr_{0.15}Au_{0.25}Pd_{0.60}$/N-$SiO_2$ concentrations at 298 K.

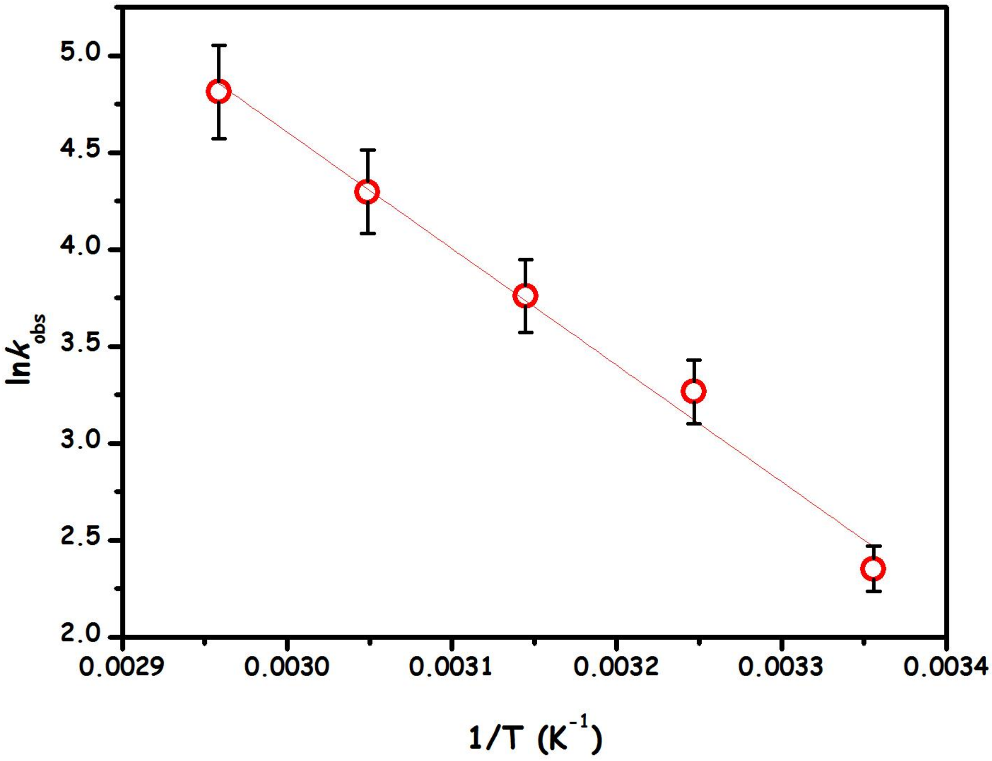

Figure S8. Arrhenius plot ($y = 22.7 - 6000\,x$ and $R^2 = 0.96$) for $Cr_{0.15}Au_{0.25}Pd_{0.60}$/N-$SiO_2$ (2.67 mM) catalyzed dehydrogenation of aqueous FA solution (0.20 M in 10.0 mL H_2O) at different temperatures.

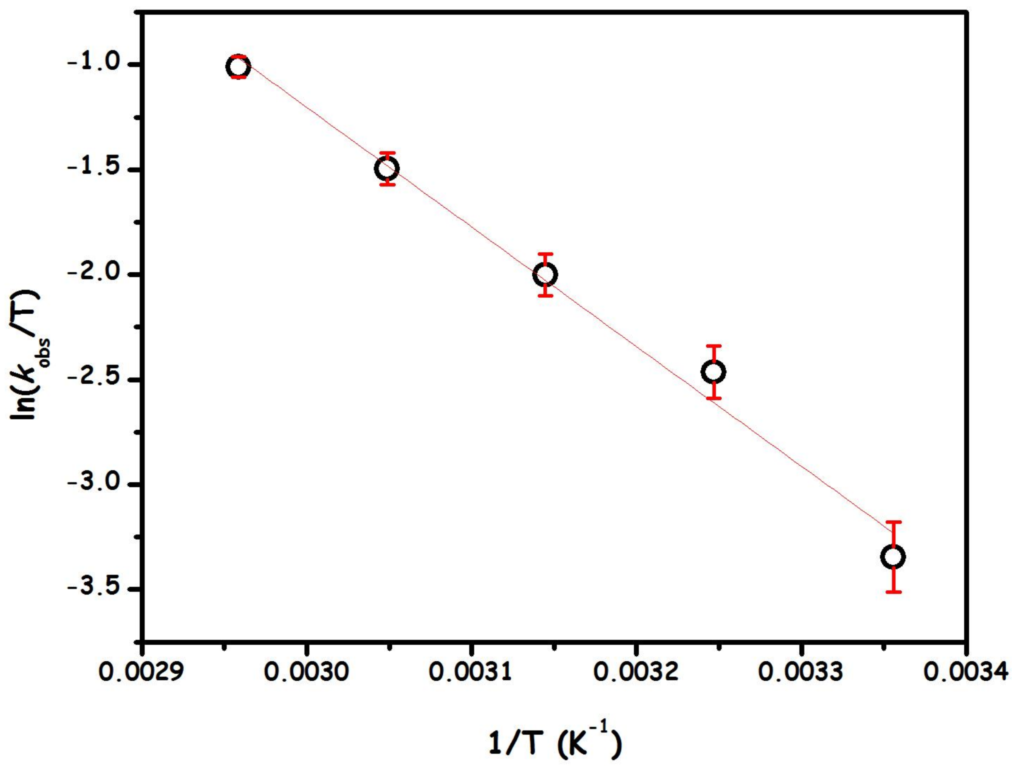

Figure S9. Eyring plot ($y = 15.9 - 5700\,x$ and $R^2 = 0.96$) for $Cr_{0.15}Au_{0.25}Pd_{0.60}$/N-$SiO_2$ (2.67 mM) catalyzed dehydrogenation of aqueous FA solution (0.20 M in 10.0 mL H_2O) at different temperatures.

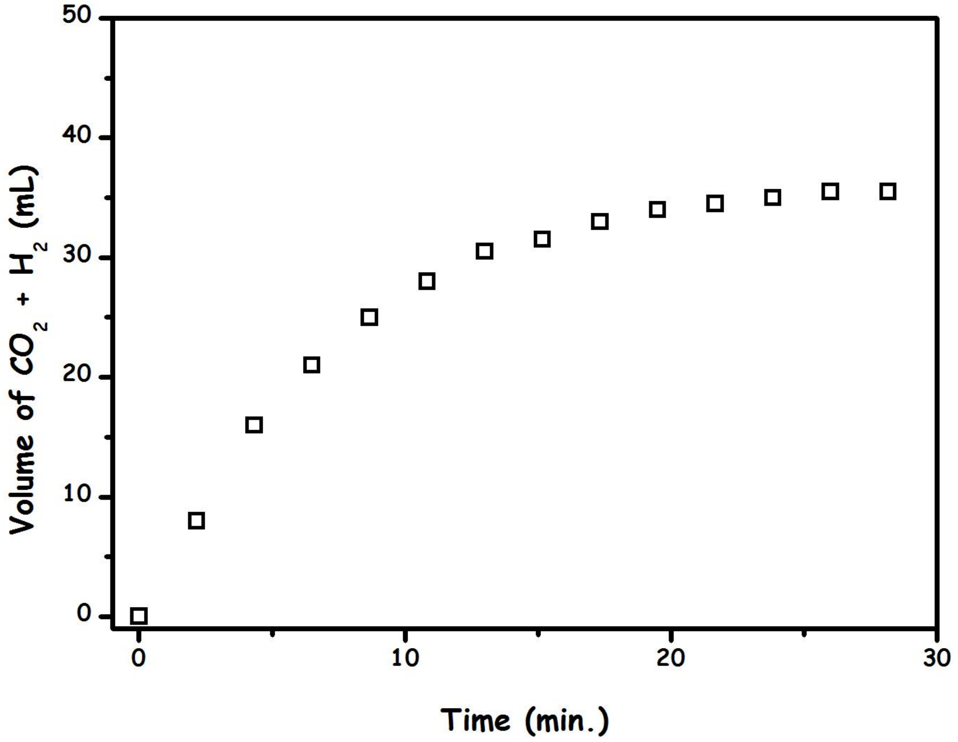

Figure S10. The volume of gas (CO_2 + H_2) (mL) versus time (min.) graph for $Cr_{0.13}Au_{0.27}Pd_{0.60}/SiO_2$ ([CrAuPd] = 4.0 mM) catalyzed dehydrogenation of aqueous FA solution (0.20 M in 10.0 mL H_2O) at 298 K.

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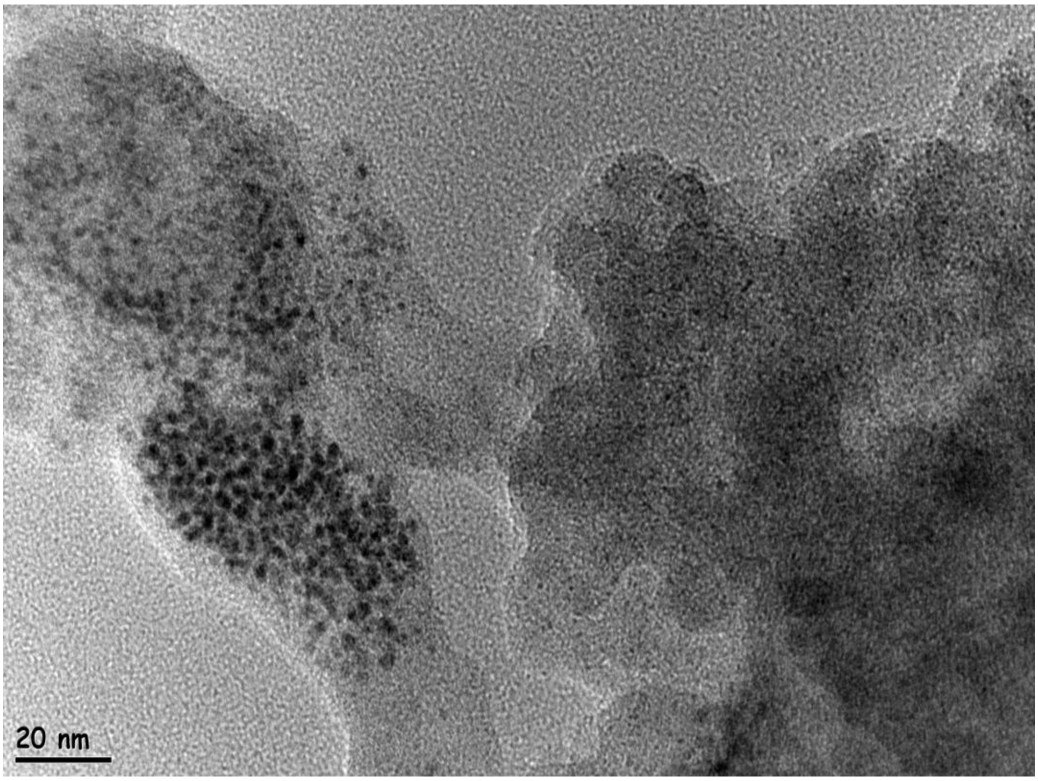

Figure S11. CTEM image of $Cr_{0.13}Au_{0.27}Pd_{0.60}/SiO_2$.

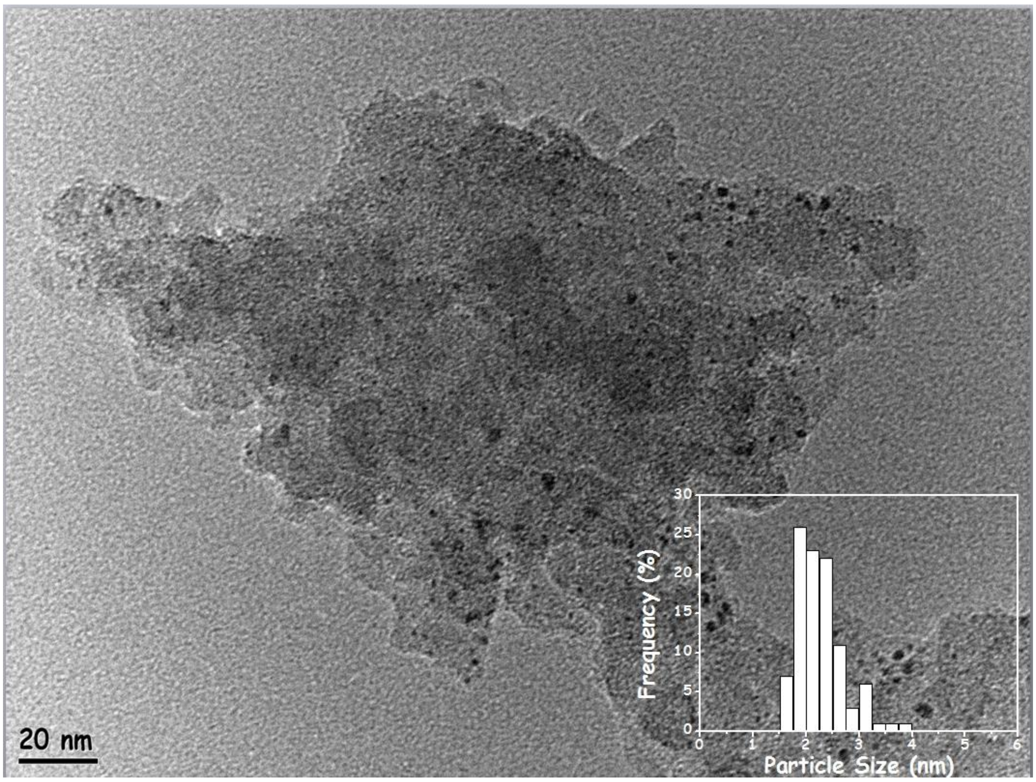

Figure S12. CTEM image and corresponding size histogram of $Cr_{0.15}Au_{0.25}Pd_{0.60}/N\text{-}SiO_2$ recovered after 5th catalytic recycle.

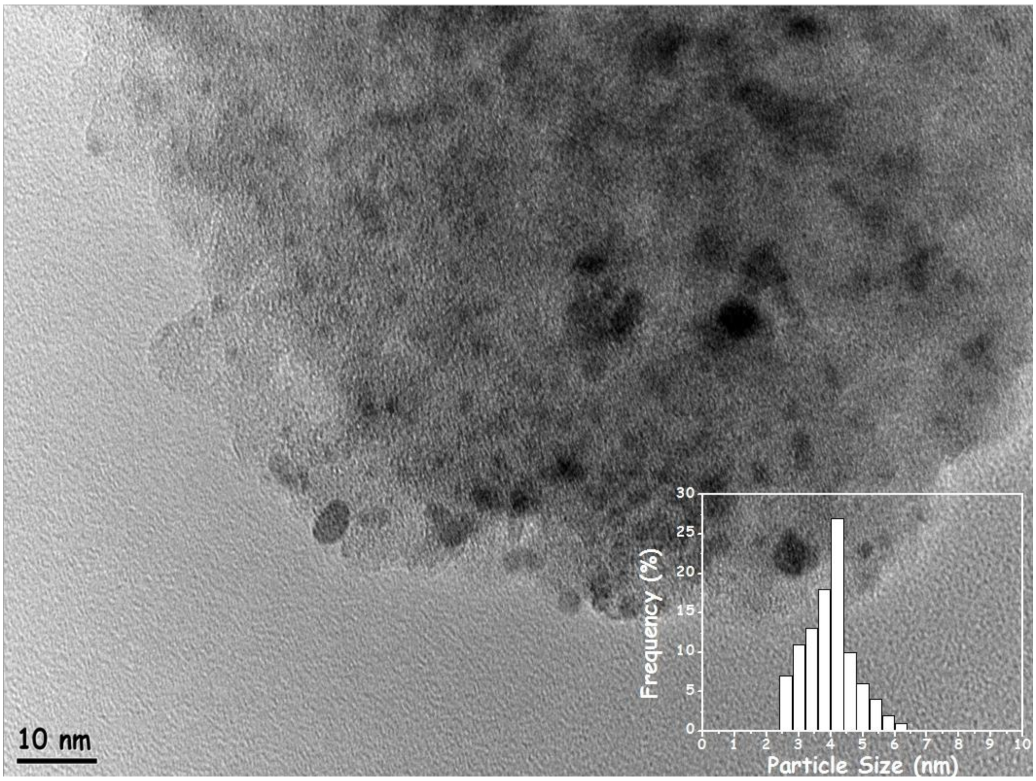

Figure S13. CTEM image and corresponding size histogram of $Cr_{0.15}Au_{0.25}Pd_{0.60}$/N-$SiO_2$ recovered after 5th catalytic reuse.

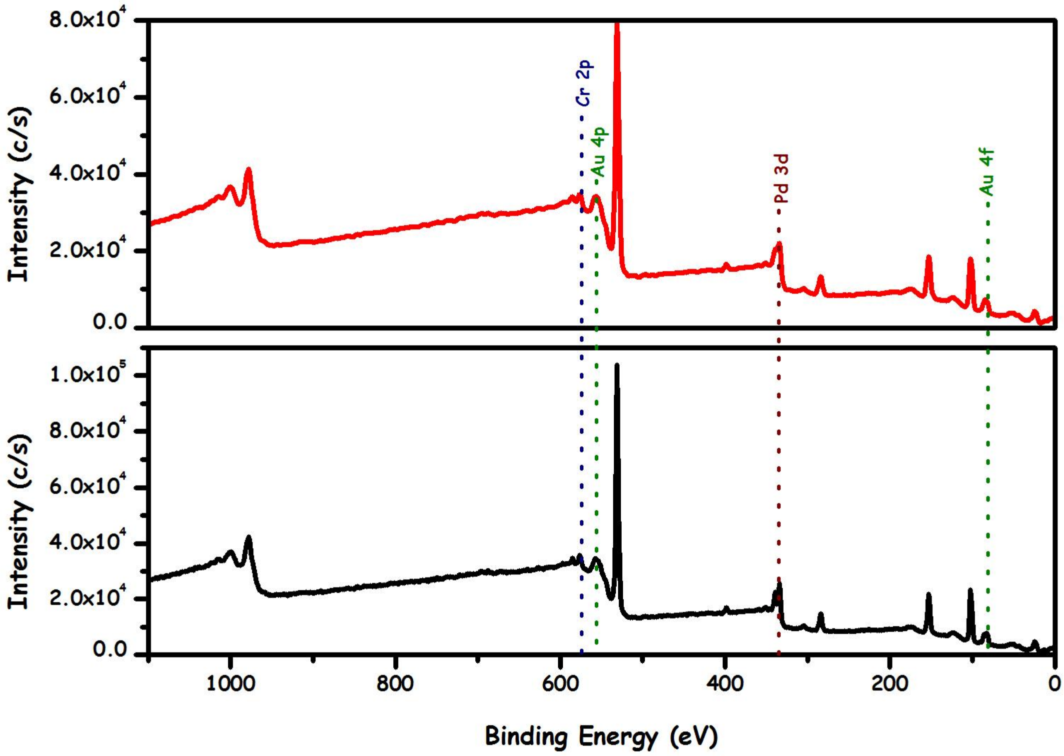

Figure S14. The survey XPS spectrum of reused (up; red) and fresh (down; black) CrAuPd/N-SiO$_2$ catalyst. The signals at 574, 340, 334.5, 86 and 82.4 eV assignable to Cr(0) (2p$_{1/2}$), Pd(0) (3d$_{3/2}$), Pd(0) (3d$_{5/2}$), Au(0) (4f$_{7/2}$) and Au(0) (4f$_{5/2}$) , respectively.[5]

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[5] C. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, Handbook of X-ray Photoelectron Spectroscopy; Physical Electronic Division, Perkin-Elmer: Waltham, MA, 1979, 44.