## **Supporting Information**

# Single Co sites in ordered SiO<sub>2</sub> channels for boosting nonoxidative propane dehydrogenation

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#### 1. Material Synthesis and Characterization.

Analytical grade Cobalt (II) chloride hexahydrate (CoCl<sub>2</sub>.6H<sub>2</sub>O), ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>), Tetraethyl orthosilicate (TEOS), ammonium hydroxide (NH<sub>3</sub>.H<sub>2</sub>O), ethanol, Hydrochloric acid (HCl), polyvinyl pyrrolidone (PVP, 30k), Hexadecyl trimethyl ammonium Bromide (CTAB), Octadearyl dimethyl ammonium chloride (1831), Sodium dodecyl sulfate (SDS) were acquired from Shanghai Chemical Reagents, China. Commercial SiO<sub>2</sub> powder (SiO<sub>2</sub> gel 60, 70-200 mesh, 470-570 m<sup>3</sup>/g) were from Alfa Aesar. Deionized water from Milli-Q System (Millipore, Billerica, MA) was used in the whole experiment.

Characterization. Powder X-ray diffraction patterns of samples were recorded on a Rigaku Miniflex-600 operating at 40 KV voltage and 15 mA current with Cu Ka radiation ( $\lambda$ =0.15406 nm). The shape and structure of the samples were examined using a Hitachi-7700 TEM operating at 100 kV. The SEM images of samples were carried out by Gemini SEM 500. The HAADF-STEM was performed on JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector working at 200 kV. The high-resolution TEM and EDS were performed on JEOL-2100F, working at 200 kV. The ICP measurements were carried out on Optima 7300 DV. Elemental analysis of Co in the solid samples were detected by inductively coupled plasma atomic emission spectrometry (Optima 7300 DV). Thermogravimetric analyses (TG and DTA) were recorded by TA SDT Q500 thermal analyzer heating from room temperature to 800 °C at the rate of 10 °C min<sup>-1</sup>. The pore parameters including Brunauer-Emmett-Teller (BET) specific surface area and pore size were obtained by evaluating of the adsorption-desorption isotherms. HK method was used to calculate the pore size distribution. These were all recorded on a Micromeritics Tristar II 3020M. X-ray photoelectron spectroscopy (XPS) was collected on scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) using Al Ka radiation and the C1s peak at 284.8 eV as internal standard. XAFS spectra at the Co K-edge were acquired at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF). The electron storage ring of SSRF was operated at 3.5 GeV with a maximum current of 250 mA. The Co K-edge XANES data were recorded in fluorescence mode. Meanwhile, Co foil, CoO, Co<sub>3</sub>O<sub>4</sub> were used as references in transmission mode.

Synthesis of silica nanomeshes (SiO<sub>2</sub> NMs). Typically, NH<sub>4</sub>VO<sub>3</sub> (10 mg) was dissolved in DI water (35 mL) to form a clear solution. Then ammonium hydroxide (1mL), CTAB (35 mg) were added slowly into the solution in sequence under magnetic stirring at 40 °C. After stirring for 15 min, TEOS (0.45 mL) was added dropwise into the solution. After that, the mixture was transferred into the 50-mL autoclave. After heating at 80 °C for 8 h, the solution was allowed to cool down to room temperature naturally. The resultant white samples were centrifuged and then washed with DI water for three times. The white CTAB/SiO<sub>2</sub> composite was obtained by freeze-drying to remove water in the sample. Subsequently, the composite was placed in a porcelain boat and heated to 550 °C (heating rate 10 °C /min) for 6 h in air, obtaining white SiO<sub>2</sub> NMs powder.

Synthesis of Co SAs/SiO<sub>2</sub> NMs. The white  $SiO_2$  NMs powder (100 mg) was dispersed in ethanol (20 mL) by sonication for 30 min. Then ammonium hydroxide

(5mL) was added to the dispersion. Subsequently,  $CoCl_2.6H_2O$  solution (10 mg/mL in ethanol) 300 µL was added dropwise under vigorous stirring. After 3 h stirring, the wathet precipitate was collected by vacuum-rotary evaporation. The as-prepared precipitate was annealed in H<sub>2</sub> (5%)/Ar atmosphere at 550 °C (heating rate 5 °C min<sup>-1</sup>) for 3 h to yield Co SAs/ SiO<sub>2</sub> NMs. Co SAs/SiO<sub>2</sub> (800 °C) NMs and Co SAs/SiO<sub>2</sub> (900 °C) NMs were obtained with the same produce of Co SAs/SiO<sub>2</sub> NMs, except that the wathet precipitate were annealed in H<sub>2</sub> (5%)/Ar atmosphere at 800 °C, 900 °C, respectively.

Synthesis of Co NPs/SiO<sub>2</sub> NMs. The white SiO<sub>2</sub> NMs powder (100 mg) was dispersed into ethanol (20 mL) by sonication for 30 min. Then ammonium hydroxide (5mL) was added to the dispersion. Subsequently, CoCl<sub>2</sub>.6H<sub>2</sub>O solution (10 mg/mL in ethanol) 3.2 mL was added dropwise under vigorous stirring. After 3 h, the mazarine precipitate was collected by vacuum-rotary evaporation. The as-prepared precipitate was annealed in H<sub>2</sub> (5%)/Ar atmosphere at 550 °C (heating rate 5 °C min<sup>-1</sup>) for 3 h to yield Co NPs/SiO<sub>2</sub> NMs.

Synthesis of Co SAs/SiO<sub>2</sub> (com). The commercial SiO<sub>2</sub> powder (100 mg) was dispersed into ethanol (20 mL) by sonication for 30 min. Then ammonium hydroxide (5mL) was added to the dispersion. Subsequently, CoCl<sub>2</sub>.6H<sub>2</sub>O solution (10 mg/mL in ethanol) 300  $\mu$ L was added dropwise under vigorous stirring. After 3 h, the wathet precipitate was collected by vacuum-rotary evaporation. The as-prepared precipitate was annealed in H<sub>2</sub> (5%)/Ar atmosphere at 550 °C (heating rate 5 °C min<sup>-1</sup>) for 3 h to yield Co SAs/SiO<sub>2</sub>(com).

Synthesis of large-scale Co SAs/SiO<sub>2</sub> NMs catalyst. Typically, NH<sub>4</sub>VO<sub>3</sub> (100 mg) was dissolved in DI water (350 mL) to form a clear solution in a 500 mL round bottomed flask. Then ammonium hydroxide (10 mL), CTAB (350 mg) were added slowly into the solution in sequence under magnetic stirring at 40 °C. After stirring for 15 min, TEOS (4.5 mL) was added dropwise into the solution. Then the temperature was rose to 80 °C under stirring. After heating at 80 °C for 8 h, the resultant white samples were centrifuged and then washed with DI water for three times. Removing water from the samples by freeze-drying, the white CTAB/SiO<sub>2</sub> composite was collected. Subsequently, the composite was placed in a porcelain boat and heated to 550 °C (heating rate 10 °C /min) for 6 h in air, obtaining white SiO<sub>2</sub> NMs powder. The white  $SiO_2$  NMs powder (5 g) was then sonicated for 30 minutes to disperse it in ethanol (200 mL). Then ammonium hydroxide (50 mL) was added to the dispersion. Subsequently, CoCl<sub>2</sub>.6H<sub>2</sub>O solution (10 mg/mL in ethanol) 3 mL was added dropwise under vigorous stirring. After 3 h stirring, the wathet precipitate was collected by vacuum-rotary evaporation. The as-prepared precipitate was annealed in H<sub>2</sub> (5%)/Ar atmosphere at 550 °C (heating rate 5 °C min<sup>-1</sup>) for 3 h to yield Co SAs/ SiO<sub>2</sub> NMs in large scale.

#### 2. Propane Dehydrogenation Activity Measurement.

Catalytic PDH reaction was performed on a fixed-bed reactor under atmospheric pressure. The inner diameter of the quartz tubular reactor is 10 mm. Catalyst (0.15 - 0.50 g) with 30–60 mesh was diluted with 0.15 g of quartz sand, loaded in the middle of the reactor. The catalyst was pretreated in N<sub>2</sub> from room temperature to 600 °C at

15 °C/min and kept for 30 min to reach steady state and remove impurities. For PDH reaction, the molar ratio of  $C_3H_8:H_2:N_2$  was 1:0:3.2, with a total flow rate of 16.8 mL/min. The weight hourly space velocity (WHSV) of propane was 2.9 h<sup>-1</sup>. To study the diffusion effect, 0.15 g or 0.30 g of catalyst with 40–50 mesh was used at various flow rates. An online gas chromatograph equipped a TCD detector channel with a 3 m TDX-1 column and a flame ionization detector (FID) channel with a KB-Al<sub>2</sub>O<sub>3</sub> capillary column (60 m×0.32 mm×10 mm) was used to analyze the products including N<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>. The propane conversion, propylene selectivity, and turnover frequency (TOF<sub>Co</sub>) were determined from the following equations:

Conversion(%) = { $[F_{in}(C_3H_8) - F_{out}(C_3H_8)]/F_{in}(C_3H_8)$ } × 100% Selectivity(%) = { $[(n_i/3) \times (F_{out}(i))]/[\Sigma_i(n_i/3) \times (F_{out}(i))]$ } × 100% TOF<sub>Co</sub> = [Conversion(%) ×  $n_{in}(C_3H_8)]/(t \times N_{Co})$ 

where i represents the hydrocarbon products in the effluent gas,  $n_i$  is the number of carbon atoms of component i,  $F_i$  is the corresponding flow rate, t is the reaction time,  $n_{in}(C_3H_8)$  is the total number of  $C_3H_8$  in the feeding gases, and  $N_{Co}$  is the number of total Co atoms in the catalyst. If we convert the coke weights to reacted  $C_3H_8$  moles, the contribution of coke is less than 0.05% in all cases. Therefore, the effect of coke on the evaluation of catalytic performances is ignored in this work.

#### 3. Computational Methods.

Density functional theory (DFT) computations were performed using a plane-wave basis set in the Vienna Ab initio Simulation Package (VASP)<sup>1</sup>. The ion-electron interaction was described with the projector-augmented-wave (PAW) method<sup>2, 3</sup>. The exchange-correlation was described by Perdew-Burke-Ernzerhof (PBE) functional and based on the generalized gradient approximation (GGA) method<sup>4</sup>. The total energy and force convergence criteria were set as  $5 \times 10^{-5}$  eV and 0.05 eV/Å, respectively. Cut-off energy for the plane wave basis set was set to 420 eV. The Brillouin zone was represented by the Monkhorst-Pack special k-point mesh of  $3 \times 3 \times 1$  for geometry optimization computations. The electron localization state of Co-3d orbitals was corrected via DFT+U method, and the value of the effective Hubbard U term was set to be 3.0 eV for Co SAs/SiO<sub>2</sub> and 3.5 eV for Co<sub>3</sub>O<sub>4</sub>, respectively. A vacuum region of 15 Å was created to ensure negligible interaction between layers. The ab initio molecular dynamic (AIMD) simulations were performed using NVT ensemble. The Nose'-Hoover method controlled simulation lasts 27 ps with a time step of 1.0 fs<sup>5</sup>. We used the DFT-D3 (D stands for dispersion) procedure to express van der Waals (vdW) interactions<sup>6</sup>. The solvation effects in aqueous solution were also considered with the Poisson-Boltzmann implicit solvation model, and the dielectric constant of water was taken as  $80^7$ .

The ab initio molecular dynamic (AIMD) simulations were performed to simulate the amorphous  $SiO_2$  computationally. During the AIMD simulations process, the cristobalite-SiO<sub>2</sub> was annealed at high temperatures and subsequently cooled down to room temperature, obtaining the amorphous SiO<sub>2</sub>, as similarly described by Huff et al<sup>8</sup> with some modifications. The lattice parameters of cristobalite-SiO<sub>2</sub> were optimized to be a = b = 4.956 Å, c=6.833 Å at PBE-D3 level. Considering the relative

displacement of atoms at constant high temperatures, the C direction was expanded by 1.2 times. A fixed volume NVT ensemble was used to conduct anneal-to-quench process from 5000 K to 300 K with a series of MD simulations, each experiment was conducted at a constant temperature, T. Initial temperature of 5000 K is chosen to melt the cristobalite-SiO<sub>2</sub>. The cooling-rate for SiO<sub>2</sub> is 153.85 K/ps for T = 3000 - 5000 K and is reducing to 111.11 K/ps when T is in the range of 100 K to 2000 K, and 40 K/ps for T=300-500 K to fully reach its equilibrium configuration. The structure obtained from previous MD simulation at a higher T is used as the input structure for the next one at a lower T. A big cell of SiO<sub>2</sub> with 108 atoms and a 20% lower density than bulk phase was maintained for all the AIMD simulations. The total simulation time is 27 ps to obtain the relatively stable amorphous-SiO<sub>2</sub>.

The Si-rich (001) facet was chose to minimize the dangling bond of Si atoms. Then, the Co atom were anchored on the  $SiO_2$  amorphous model to simulate the Co-O coordination environment, and the Co-O<sub>3</sub> sites on the amorphous model were built through precisely adjusting position of Co sites and bond length of the Co-O bond to meet the experimental results.

Finally, we calculated the Gibbs free energy for PDH reaction process according to computational hydrogen electrode (CHE) model<sup>9</sup> and it can be computed by:

$$\Delta G = \Delta E + \Delta E_{ZPE} - \Delta TS + \Delta GpH + \Delta G_{U}$$

where  $\Delta E$  is the computed reaction (electronic) energy, T is system temperature, and  $E_{ZPE}$  and S are zero-point energy and entropy, respectively. The effects of pH and electrode potential (U) can be treated as:  $\Delta GpH = 0.0592 \times pH$  and  $\Delta G = -eU$ .

#### 4. Supporting Figures and Tables.



**Figure S1:** TEM images of the products obtained at different time. (a) 5 min (b) 10 min (c) 30min (Inset is the schematic diagram) (d) the magnification figure of (c), (e) 1 h (f) 3 h (g) 5 h (h) 8 h. The nanosheets in Figure S1d consist of wires about 10 nm in diameter, which is similar to the diameter of nanochains in Figure S1b, confirming that the sheets are assembled from nanochains.



**Figure S2:** Simulated growth process diagram of  $SiO_2$  NMs. (a), (b), (c), (d) the simulated diagram of the corresponding products in figure S 1a, S 1b, S 1c, S 1h, respectively.



**Figure S3:** TEM images of the CTAB/SiO<sub>2</sub> composite obtained with varying amount of CTAB: (a) 0 mg, (b) 20 mg, (c) 50 mg, and (d) 100 mg.



**Figure S4:** TEM images of the CTAB/SiO<sub>2</sub> composite obtained with different amount of ammonium hydroxide: (a) 0.1 mL, (b) 1.5 mL, (c) 3 mL, (d) 5 mL.



**Figure S5:**  $CTAB/SiO_2$  composite prepared by adding different volume of TEOS: (a) 0.1 mL, (b) 1 mL, (c) 2 mL, (d) 5 mL.



Figure S6: TEM images of the  $CTAB/SiO_2$  composite prepared using various amount of  $NH_4VO_3$ : (a) 5 mg, (b) 20 mg, (c) 50 mg, (d) 100 mg.



**Figure S7:** TEM images of the samples prepared by using different surfactants: (a) F127, (b) PVP, (c) 1831, (d) SDS.



**Figure S8:** TEM images of the Samples prepared by heating treatment at different temperature: (a) 60 °C, (b) 80 °C, (c) 100 °C, (d) 150 °C.



Figure S9: (a) low-magnified SEM images of  $CTAB/SiO_2$  composite. (b-d) TEM images with different magnifications.



Figure S10: (a) FT-IR spectra of SiO<sub>2</sub> NMs and CTAB/SiO<sub>2</sub> composite. The IR spectrum showed that the CTAB/SiO<sub>2</sub> composite contained the surfactant molecules and the absorbed water. For SiO<sub>2</sub> NMs, the peaks centered at 3300-3500 and 1633 cm<sup>-1</sup> were arose from stretching vibrations of -OH and water molecules absorbed on the sample surface<sup>10</sup>. The spectrum of SiO<sub>2</sub> showed two bands around 1088 cm<sup>-1</sup> and 800 cm<sup>-1</sup>, which were attributed to the Si–O–Si asymmetric bond stretching vibration. The peak at 960 cm<sup>-1</sup> and 466 cm<sup>-1</sup> could be assigned to Si-OH stretching vibration, Si-O-Si bending vibration, respectively. For CTAB/SiO<sub>2</sub> composite, the peaks at 2855 cm<sup>-1</sup> and 2922 cm<sup>-1</sup> were owing to the stretching vibrations of -CH<sub>2</sub> and-CH<sub>3</sub> in CTAB<sup>11</sup>. Also, the strong amplitudes of Si–O–Si at 1088 cm<sup>-1</sup> in SiO<sub>2</sub> NMs were split into two peaks at 1067 and 1272 cm<sup>-1</sup> in vinyl functionalized CTAB/SiO<sub>2</sub> composite. The peaks at 1400-1500 cm<sup>-1</sup> could be attributed to the C-H bending vibration of CTAB. The above results suggested that CTAB is presented in the CTAB/SiO<sub>2</sub> composite. (b) TG profiles of SiO<sub>2</sub> NMs and CTAB/SiO<sub>2</sub> composite with a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub>. The first weight loss step at 38-284 °C was corresponded to the loss of adsorbed and interlayer water, whereas the subsequent second major weight loss at 284 to 600 °C was due to the decomposition of the grafted CTAB molecules of CTAB/SiO<sub>2</sub> composite in figure S10 (b). The SiO<sub>2</sub> NMs nearly had no weight loss after removing adsorbed water at 41-108 °C, indicating excellent thermal stability.



Figure S11: (a) SEM and (b-c) TEM images of  $SiO_2$  NMs with different magnifications. (d) SAED pattern of  $SiO_2$  NMs.



Figure S12: (a)  $N_2$  adsorption-desorption isotherms and (b) the corresponding pore size distribution curves for obtained SiO<sub>2</sub> NMs.



Figure S13: Schematic illustration for the synthesis of Co SAs/SiO<sub>2</sub> NMs catalyst.



Figure S14: (a-c) The color of  $SiO_2$  NMs, Co SAs/SiO<sub>2</sub> NMs, and Co NPs/SiO<sub>2</sub> NMs, respectively.



Figure S15: (a-b) TEM images of Co NPs/SiO<sub>2</sub> NMs.



**Figure S16:** (a) XRD patterns of Co NPs/SiO<sub>2</sub> NMs. (b) XPS spectra of survey scan, (c) Co 2p regions of Co NPs/SiO<sub>2</sub> NMs. The fitting peaks for Co  $2p_{3/2}$  could be ascribed to Co (III) (779.2 eV)<sup>12</sup> and Co(II) (780.8 eV)<sup>13, 14</sup>, respectively, the Co NPs/SiO<sub>2</sub> NMs possessed a Co((III)/Co(II) surface molar ratio of 1.6, confirming that the mainly CoO<sub>x</sub> species exited at the surface is Co<sub>3</sub>O<sub>4</sub>.



**Figure S17:** XPS spectrum of (a) survey scan, (b) Si 2p regions (c) O 1s regions of SiO<sub>2</sub> NMs; (d) survey scan, (e) Si 2p regions (f) O 1s regions of Co SAs/SiO<sub>2</sub> NMs.



Figure S18: H<sub>2</sub>-TPR profiles of Co SAs/SiO<sub>2</sub> NMs, Co SAs/SiO<sub>2</sub> (com).



Figure S19: (a-b) TEM image of the Co SAs/SiO<sub>2</sub> (com).



**Figure S20:** (a) HAADF-STEM images of Co SAs/SiO<sub>2</sub> (com), indicating that only Co single atoms are present in Co SAs/SiO<sub>2</sub> (com). (b) XRD pattern of Co SAs/SiO<sub>2</sub> (com) showed no characteristic peaks of bulk Co. (c) XPS spectrum of Co SAs/SiO<sub>2</sub> (com).



Figure S21: EPR of SiO<sub>2</sub> (com) and Co SAs/SiO<sub>2</sub> (com).



**Figure S22:** EPR spectra of the catalysts obtained at different condition with  $H_2/Ar$  (5%/95%) atmosphere.



**Figure S23:** (a, b) TEM images of Co SAs/SiO<sub>2</sub> NMs obtained by annealing in  $H_2$  (5%)/Ar at 800 °C, 900 °C for 3h. The original shape of mesoporous nanosheets remains with no collapsing.



**Figure S24:** (a, b) N<sub>2</sub> adsorption-desorption isotherms and the corresponding pore size distribution curves for as-synthesized Co SAs/SiO<sub>2</sub> NMs obtained by annealing in H<sub>2</sub>(5%)/Ar at 800 °C, 900 °C for 3h.



**Figure S25:** (a) HAADF-STEM images of Co SAs/SiO<sub>2</sub> (900 °C) obtained by annealing in H<sub>2</sub> (5%)/Ar at 900 °C for 3 h, indicating that only Co single atoms were presented in Co SAs/SiO<sub>2</sub> (900 °C). (b) XRD pattern of Co SAs/SiO<sub>2</sub> (900 °C) showed no characteristic peaks of bulk Co.



**Figure S26:** EXAFS fitting curves at R space of Co SAs/SiO<sub>2</sub> (800 °C) NMs and Co SAs/SiO<sub>2</sub> (900 °C) NMs.



**Figure S27:** (a) HAADF-STEM images of Co NPs/SiO<sub>2</sub> (com) obtained by annealing in H<sub>2</sub> (5%)/Ar at 700 °C for 3h, indicating that Co single atoms and clusters coexist on the commercial SiO<sub>2</sub> carrier. (b) the intensity profile of yellow rectangle displayed that Co sites were separated by around 0.18 nm (Figure 2g), which was less than the lattice distance of Co (100) facet ( $d_{100} = 0.22$  nm), indicating the existence of Co<sub>x</sub> species. (c) the intensity profile of yellow dash line displayed a Co<sub>x</sub> cluster of about 1.16 nm, indicating the existence of Co<sub>x</sub> species.



**Figure S28:** (a) Propane conversion, propane selectivity over Co SAs/SiO<sub>2</sub> NMs at different  $C_3H_8:N_2:H_2$  ratio. Reaction conditions: 75 mg catalyst, 550 °C, WHSV  $(C_3H_8) = 2.9 \text{ h}^{-1}$ . (b) Propane conversion, propane selectivity over Co SAs/SiO<sub>2</sub> PNS with different amount of catalyst. Reaction conditions: 550 °C,  $C_3H_8:N_2 = 2:6.4$ , WHSV  $(C_3H_8) = 2.9 \text{ h}^{-1}$ .



**Figure S29:** (a) Atomic selectivity to  $C_1$ - $C_3$  products over Co SAs/SiO<sub>2</sub> NMs, (b) Atomic selectivity to  $C_1$ - $C_3$  products over Co NPs/SiO<sub>2</sub> NMs.



**Figure S30:** (a) Atomic selectivity to  $C_1$ - $C_3$  products over Co SAs/SiO<sub>2</sub> (com), (b) Atomic selectivity to  $C_1$ - $C_3$  products over SiO<sub>2</sub> NMs.



**Figure S31:** (a) Catalytic activity, 24 h stability of the Co SAs/SiO<sub>2</sub> NMs. (b) The conversion of propane and selectivity of propylene over Co SAs/SiO<sub>2</sub> NMs catalyst after several regeneration cycles. reaction condition: 0.15 g of catalyst,  $C_3H_8$ : N<sub>2</sub>=1:3.2, WHSV = 2.9 h<sup>-1</sup>, 550 °C. After the completion of one cycle, the catalyst was calcinated at 600 °C for 3 h under air atmosphere to remove the carbon deposition.



**Figure S32:** (a) TEM image, (b) Magnified HAADF-STEM image of Co SAs/SiO<sub>2</sub> NMs catalyst after durability test.



**Figure S33:** (a) Nitrogen adsorption-desorption isotherm and (b) corresponding pore size distribution curve of Co SAs/SiO<sub>2</sub> NMs after 24 h durability test.



**Figure S34:** (a) The XRD pattern and (b) The EXAFS fitting curve for Co SAs/SiO<sub>2</sub> NMs after durability test.



**Figure S35:** (a) TGA curves (b) Raman spectra of the Co SAs/SiO<sub>2</sub> NMs (spent) catalysts after 24 h PDH reactions and Co SAs/SiO<sub>2</sub> NMs. TGA analysis was performed to provide the amount of coke formed on the spent catalysts. The coke amount on the spent Co SAs/SiO<sub>2</sub> NMs catalyst was estimated as 6.8 wt%, as shown in the thermal weight loss curves in Figure R5a. Typical signals of coke species of the D band and the G band, could be distinguished in the Raman spectra of Co SAs/SiO<sub>2</sub> NMs (spent) as shown in Figure R6b<sup>15</sup>. In a detailed interpretation, for Co SAs/SiO<sub>2</sub> NMs (spent), the most intense G band, at 1595 cm<sup>-1</sup>, responded to the perfect graphite lattices. An intense D<sub>1</sub> band, at 1340 cm<sup>-1</sup>, originated from double-resonant Raman scattering of the graphene lattices with defects and in-plane transverse optic phonon modes. The D<sub>2</sub> band located at 1640 cm<sup>-1</sup> was ascribed to E<sub>2g</sub> symmetry vibration of disordered graphitic lattices<sup>16, 17</sup>. The D<sub>3</sub> band at 1495 cm<sup>-1</sup> was attributed to disordered graphitic lattices with A1g symmetry, while the D<sub>4</sub> band at 1220 cm<sup>-1</sup> was assigned to amorphous carbon.



**Figure S36:** (a) Picture of  $\sim$ 5 g of the Co SAs/SiO<sub>2</sub> NMs catalyst. (b) the performance test of the amplified Co SAs/SiO<sub>2</sub> NMs catalyst.



Figure S37: The simulation of the cooling curve of cristobalite-SiO<sub>2</sub> to obtain the amorphous SiO<sub>2</sub>.

The ab initio molecular dynamic (AIMD) simulations were performed to simulate the amorphous SiO<sub>2</sub> computationally. At the temperature of 5000 K, the crystal structure of cristobalite-SiO<sub>2</sub> is completely broken. The cooling-rate for SiO<sub>2</sub> is 153.85 K/ps for T = 3000 - 5000 K and is reducing to 111.11 K/ps when T is in the range of 100 K to 2000 K, and 40 K/ps for T=300-500 K. The total simulation time is 27 ps to obtain the relatively stable amorphous SiO<sub>2</sub>.



Figure S38: The simulation structure transformation of cristobalite-SiO<sub>2</sub> to the amorphous SiO<sub>2</sub>.



Figure S39: The Bader charge and the fitted oxidation states of Co SAs/SiO<sub>2</sub> NMs.

Sample	Shell	Ν	R (Å)	σ <sup>2</sup> *10 <sup>3</sup> (Å <sup>2</sup> )	R-factor (%)
CoO	Co-O	6.0	2.13	/	/
	Co-O	3.2±0.2	2.05±0.01	8.88±0.73	1.2
C0 SAS/SIO <sub>2</sub> NMS	Co-Co	< 0.3	/	/	/
Co SAs/SiO <sub>2</sub> NMs	Co-O	3.4±0.2	2.06±0.01	6.5±0.6	0.2
(800 °C)	Co-Co	< 0.3	/	/	/
Co SAs/SiO <sub>2</sub> NMs	Со-О	3.3±0.3	2.07±0.01	6.68±0.79	1.2
(900 °C)	Co-Co	< 0.3	/	/	/

**Table S1.** Co K-edge EXAFS curves fitting parameters:  $\Delta k = 3.0 - 11.0 \text{ Å}^{-1}$ ,  $\Delta r = 1.0 - 3.0 \text{ Å}$ .

N, coordination number; R, distance between absorber and backscatter atoms;  $\sigma^2$ , Debye-Waller factor to account for both thermal and structural disorders; R-factor (%) indicate the goodness of the fit.

**Table S2.** The comparison between the EXAFS results and the DFT results of the Co single site.

Data	Bond	Ν	R (Å)
FT-EXAFS results	Co-O	3.2±0.2	2.05±0.01
DFT results	Co-O	3	1.99

 Table S3 Summary of the catalytic data of representative non-noble metal-based catalysts used in

 PDH.

Catalysts	Temperature/	WHSV	Conversion	Selectivity	Lifetime	Formation rate/	TOF/	Dof	
	٥C	/ <b>h</b> -1	/%	/%	/h	$mol_{C3H6}g_{C0}^{-1}h^{-1}$	h-1	Kei.	
Co SAs/SiO2 NMs	550	2.9	25-21.2	95.1-90.9	24	3.16	196	This	
								work	
	550	2.9	18-16	81.4-83.4	8	0.83	49	This	
Co SA\$/SIO <sub>2</sub> (com)								work	
	550	2.9	5.7-7	87-84.6	8	0.22	13	This	
CU NES/5102 MAIS	330							work	
Co/H-ZSM5	500	-	-25	-60	-	-	-	18	
Co/Al <sub>2</sub> O <sub>3</sub>	560	0.43	25.7-21.8	83.6-81.6	6	0.014	-	19	
Co/SiO <sub>2</sub>	550	6.38	7.3-4.1	88.15-84.46	10	0.0093	18	20	
Co-Al <sub>2</sub> O <sub>3</sub> -HT	590	2.9	23	97	5	0.3	-	21	
Co/Al <sub>2</sub> O <sub>3</sub> -NS	550	0.98	14.4-7.7	92.7-90.5	12	0.057	-	22	
1-Fell	650	0.18	4.9-6.3	99	18	0.0002	1.1	23	
(3Fe:P)/Al <sub>2</sub> O <sub>3</sub>	600	0.27	15-12	80	5.33	0.01	19	24	
NiMo-C12	400	5.5	18.2	63.8		-	-	25	
Mo-V-O	500	-	36	89	16	0.0069	-	26	
Pt-ZnO/Al <sub>2</sub> O <sub>3</sub>	600	3	35-31	94-97	4	0.075		27	
Zn/SiO <sub>2</sub>	550	0.18	-	95	12	0.000028	0.772	28	
Cr-Al-800	600	8.63	33.2-20.4	90.4-84.7	15	0.48		29	
6 wt%VOx/g-A <sub>12</sub> O <sub>3</sub>	600	8.25	25-15	72-80	-	0.563		30	
3 wt%VO <sub>x</sub> /SiBeta	600	0.59	38-23	88-94	16	0.15	108	31	
Ni <sub>3</sub> Ga/Al <sub>2</sub> O <sub>3</sub>	600	2.16	13-9	94-81	82	0.006	169	32	
Ga/H-MFI	460	0.0025	9	82.6-82.3	6.67	-	-	33	
$\gamma  \text{Ga}_2\text{O}_3/\text{SiO}_2$	550	7.2	30.2-3.2	88-65	100 min	0.16	-	34	
ZrO <sub>2</sub>	550	1.57	30	83	35	0.008	-	35	
Cr20Zr80/SiO <sub>2</sub>	550	34.5	30	85	25	0.054	72	36	

PSC MoN	500	-	12	97	46.8	-	46.8	37

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