# **Supporting Information for**

Enhancing Room-Temperature CO Oxidation via Encapsulation of Bimetallic PtNi Clusters within Mesoporous Silicate-1 Catalyst

Ronghua Cui<sup>1,#</sup>, Siyuan Yang<sup>1,#</sup>, Zejian Dong<sup>1</sup>, Lifeng Zhang<sup>1</sup>, Xing Chen<sup>1,2</sup>, Langli

 $Luo^{1,2*}$ 

<sup>1</sup>Institute of Molecular Plus, Department of Chemistry, Tianjin University, Tianjin

300072, China

<sup>2</sup>Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

Corresponding Authors: L. Luo (luolangli@tju.edu.cn)

## **Materials and Methods**

For the synthesis of nanostructures, Ni (NO<sub>3</sub>)<sub>2</sub> (Ni (II) nitrate  $\geq$  97% purity) and H<sub>2</sub>PtCl<sub>6</sub> ( $\geq$  99% purity) were purchased from Shanghai Titan Technology. Potassium hydroxide (KOH, Meryer, 95%), tetraethylorthosilicate (TEOS, 28 wt%), tetrapropylammonium hydroxide solution (TPAOH, 40 wt% in water), and ethylenediamine (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>,  $\geq$  99.0%) were purchased from Greagent. All syntheses of nanostructures were performed using the solvothermal method.

#### 1. Synthesis of PtNi@S-1, Pt@S-1, and Ni@S-1.

**1.1 Synthesis of Pt@S-1.** In this study, we used a modified solid crystallization method to synthesize Pt@S-1 catalyst. Compared with the reported solid crystallization method to synthesize zeolite catalyst, we changed the temperature and environment of TEOS hydrolysis. First, 8.23 g TEOS was dropped into 30 ml of deionized water with vigorous stirring at 1000 rpm, and the solution became turbid after full mixing. A solution of 2 ml 2 M KOH was added to the aqueous solution and completely hydrolyzed at 80 °C until the solution was clear. Mix the solution and continuous stirring at 1000 rpm for 2 h. The H<sub>2</sub>PtCl<sub>6</sub> with 3 ml ethylenediamine (EDA) solution was mixed with 0.1 g PVP and stirred for 30 min at the same rotational speed. Slowly add this solution dropwise to hydrolysate, and no precipitates were observed under stirring for 3 h. The dispersion was stirred and dried at 70 °C for about 5 hours for the complete removal of water; the dry gel was then collected and ground into powders, and the as-prepared dry gel powders were further transferred to a Teflon-lined autoclave for crystallization at 120 °C for 72 h with the assistance of 3 ml of

TPAOH. The as-synthesized solid product was centrifuged, washed with water several times, and then dried at 90 °C in the oven overnight, followed by calcination in air and 10 vol%  $H_2/Ar$  at 550 °C for 2 h respectively.

**1.2 Synthesis of Ni@S-1.** We synthesized the catalyst similarly to Pt@S-1, with Ni  $(NO_3)_2$  added to the gel as one of the metal species.

**1.3 Synthesis of PtNi@S-1.** We synthesized the catalyst in the same way as Pt@S-1. The ratio of the molar amounts of Pt and Ni added is 3:1. The schematic diagram of the catalyst synthesis is shown below.



Schematic of synthesis routes of Pt/Ni@S-1 catalyst.

## 2. Materials Characterizations.

**2.1 Scanning electron microscope (SEM)** analysis was performed at Thermo Scientific<sup>TM</sup> Apreo at an acceleration voltage of 5 kV.

**2.2 Transmission electron microscopy (TEM)** and energy dispersive X-ray spectrometry (EDXS) measurements were performed on Thermo Scientific<sup>TM</sup> Talos F200X with an accelerating voltage of 200 kV.

**2.3 X-ray diffraction (XRD)** patterns were obtained by a Rigaku Smartlab 9KW equipped with Cu K $\alpha$  ( $\lambda = 0.15406$  nm) from 5° to 60° with 10°/min.

2.4 X-ray photoelectron spectra (XPS) were performed on ESCALAB-250Xi

(Thermo Fisher) using Al K $\alpha$  radiation as the X-ray source to obtain the binding energies and oxidation states.

We measured the loadings of both Pt and Ni in the as-prepared samples by an inductively coupled plasma optical emission spectrometer((ICP-OES). The specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distributions of micropores and mesopores were calculated by the Horvath-Kawazoe (HK) and Barret-Joyner-Halenda (BJH) methods, respectively. The total pore volume of each catalyst was accumulated at a relative pressure of  $P/P^0 = 0.99$ .

**2.5** CO/O<sub>2</sub> temperature-programmed desorption (CO/O<sub>2</sub>-TPD) measurements were performed on an Auto Chem II 2920 automatic catalyst characterization system. First, 100 mg of a sample was loaded into a U-shape quartz reactor and purged with He at 473 K for 2 h to remove adsorbed carbonates and hydrates. After cooling to 323 K, CO gas was introduced for 1 h to saturation and then switched to He for 1 h to remove the weakly physically adsorbed CO on the surface. The sample was heated to 973 K at a ramping rate of 10 K min<sup>-1</sup> in He, and the outgassing was detected by TCD. O<sub>2</sub>-TPD have the same principle as the above process, adsorbed gases of 5 vol% O<sub>2</sub>/He, respectively. The samples were reduced in a gas mixture of 10 vol% H<sub>2</sub>/Ar at 550°C for 2 h.

CO-pulse adsorption was used to determine the amount of exposed Pt and Ni atoms on the chemisorption analyzer mentioned above. 50 mg as-prepared samples were pretreated in 100 mL/min 10% CO/Ar for 90 min at 550 °C (for Pt/Ni@S-1),

and then switched to He and ramped to 700 °C to degas for 30 min and then cooled down to 0 °C. CO was dosed on the samples every 2.5 min until saturation.

2.6 In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) experiment was performed at the Harrick HVC high-temperature transmission cell in the range of 400 - 4000 cm<sup>-1</sup>. The section applies to a Thermo Nicolet Nexus FTIR spectrometer allocated with a mercury cadmium telluride (MCT) detector. For the *in situ* DRIFTS of CO adsorption experiment, the catalyst was firstly pretreated in an H<sub>2</sub> atmosphere (10 vol% H<sub>2</sub>/Ar, 30 ml min<sup>-1</sup>) at 550 °C to reduce the catalyst for 2 h. Then, pure Ar was introduced into the cell for 30 min to remove the remaining H<sub>2</sub> in the cell and the adsorbed H<sub>2</sub> on the catalyst. The background spectra were recorded during cooling to room temperature. For the in situ experiments, the gas mixture (5 vol% CO in Ar, 30 ml min<sup>-1</sup>) was introduced into the cell for 30 min at 25 °C. Thereafter, pure Ar was introduced to remove physically adsorbed CO and collect the spectra.

2.7 X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra, were performed at the BL14W1, Shanghai Synchrotron Radiation Facility (SSRF), China. Si (111) and Si (311) -crystal monochromators were used for energy selection of the L<sub>3</sub>-edge of Pt and K-edge of Ni, respectively. The Pt L<sub>3</sub>-edge was recorded at room temperature in the transmission or fluorescence mode, based on the energy calibration of Pt foil. Before the measurement, the sample was reduced in situ in 10 vol%  $H_2/Ar$  for 2 h at 550 °C and then cooled to room temperature for data collection.

The data were analyzed by the Athena software packages [1,2].

**3. Catalytic Performance Testing.** Catalytic properties of PtNi encapsulated in S-1 zeolite toward CO oxidation were tested and compared to pure Pt@S-1 and Ni@S-1. SiO<sub>2</sub> is inert to the oxidation of carbon monoxide, which allows us to measure the activity of metal clusters independent of support effects. We used a gas ratio of 1% CO and 20% O<sub>2</sub>/Ar to simulate an atmospheric environment and tested the CO oxidation reaction at 60,000 mL·g<sup>-1</sup>·h<sup>-1</sup>.

**4. Theoretical Calculations.** All of the energy calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [3] with generalized gradients approximation (GGA) of Perdew-Bruke-Ernzerhof (PBE) [4] functional. We used the small Pt13 and Pt12Ni1 clusters and a portion of the zeolite-10 MR frame as the computational models to support the metal clusters. The length of the periodic box is 20 Å for 3 directions. The plane-wave basis set was used, and the cutoff energy was 400 eV. During the simulations, a single gamma point was sampled for Brillouin zone integration [5]. All the calculations were spin-polarized, and the convergence criteria for the electronic structure and the geometry were set to  $10^{-5}$  eV and 0.02 eV/Å.

The adsorption energy for CO and O<sub>2</sub> was calculated by:

 $E_{ads} = E_{catalyst@adsorbate} - E_{catalyst} - E_{adsorbate}$ 

## **Supplementary Figures**



**Figure S1.** The XRD of fresh catalysts of Pt@S-1, Ni@S-1 and PtNi@S-1. The figure shows no characteristic peaks for Pt and Ni, indicating that the metals Pt and Ni are well dispersed in the zeolite.



**S2.** N<sub>2</sub> adsorption-desorption isotherms and pore size distribution analysis based on BJH adsorption branch of Pt@S-1, PtNi@S-1 and Ni@S-1.



Figure S3. The HAADF-STEM elemental analysis of PtNi@S-1. Pt: orange, Ni: purple.



Figure S4. The HAADF-STEM elemental analysis of Pt@S-1 and Ni@S-1. Pt:orange,

Ni: purple. The purple Ni is the mapping of left Ni@S-1. The orange Pt is the mapping of left Ni@S-1.



**Figure S5.** STEM-HAADF images (**a**, **c**, **e**) of fresh catalysts of Pt@S-1, Ni@S-1 and PtNi@S-1 and corresponding fast Fourier transformation (FFT) patterns (**b**, **d**, **f**). White and yellows circles in (**b**) and (**d**) indicate different orientations of sub-grains in zeolite particles.



**Figure S6.** STEM image of PtNi@S-1 with metal clusters around 1 nm in size. The contrast between light and dark indicates that the catalyst has uniform mesopores.



**Figure S7.** The HAADF-STEM figures of catalyst (a, b) op-PtNi@S-1: bimetallic PtNi@ zeolite catalysts synthesized by the one-pot method. (c)The HAADF-STEM elemental analysis of op-PtNi@S-1. Ni: red, Pt: yellow. (d) CO conversion of Pt@S-1, PtNi@S-1, op-PtNi@S-1 catalysts for CO oxidation reaction (1% CO and 20% O<sub>2</sub>

balanced in Ar with a space velocity is 60000 mL $\cdot$ g<sup>-1</sup>·h<sup>-1</sup>).



**Figure S8.** STEM image of Pt/Ni@S-1. (a)Pt3Ni0.3@S-1 means that the ratio of PtNi is 3:0.3. (b)Ni0.3@S-1 means monometallic@zeolite catalyst with Ni loading of 0.3%. (c)Pt3Ni3@S-1 and (d)Ni3@S-1 ditto. (e ,f)The size distribution charts of encapsulated metals in Pt3Ni0.3@S-1, and Pt3Ni3@S-1.



Figure S9. Catalytic performance for the CO oxidation reaction. CO conversion

of Pt@S-1, PtNi@S-1, Pt3Ni3@S-1 and Pt3Ni0.3@S-1 catalysts for CO oxidation reaction (1% CO and 20%  $O_2$  balanced in Ar with a space velocity is 60000 mL·g<sup>-1</sup>·h<sup>-1</sup>)



**Figure S10.** Stability test of CO conversion rate for the PtNi@S-1. (1% CO and 20%  $O_2$  balanced in Ar, the space velocity is 60000 mL g<sup>-1</sup> h<sup>-1</sup>). To study the stability of PtNi@S-1 more convincingly, we made this catalyst CO 100% conversion at 60 °C for 10 h. After 10 h, after cooling and stabilizing for one hour, the activity at each temperature point could be maintained unchanged from the original test.



Figure S11. Stability test of CO conversion rate for the PtNi@S-1.



Figure S12. Stability test of CO conversion rate for the Pt@S-1 at 60°C.



Figure S13. The fluctuation of CO conversion rate of Pt@S-1 catalyst at 30~60°C range.



Figure S14. O1s XPS spectra of Pt@S-1, Ni@S-1 and PtNi@S-1.



**Figure S15.** Comparison of absorption peaks for PtNi@S-1, Ni@S-1 and Pt@S-1 catalysts after the saturation of CO molecules for 20 minutes.



**Figure S16.** In situ DRIFTS study of CO adsorption during 2.5% CO/Ar purging on Ni@S-1.



**Figure S17.** The corresponding Pt L<sub>3</sub>-edge and Ni K-edge EXAFS fitting curves for Pt/Ni@S-1 catalysts at R-space, respectively. (a) PtNi@S-1 (b) Pt@S-1 (c) Ni@S-1.



Figure S18. The Pt L<sub>3</sub>-edge and Ni K-weighted k<sup>3</sup>-weighted EXAFS Fourier transforms of the Pt/Ni@S-1 samples. (a) PtNi@S-1 (b) Pt@S-1 (c) Ni@S-1.





**Figure S19.** XAS spectra of Pt foil, PtO<sub>2</sub>, Pt@S-1, PtNi@S-1, Ni foil, Ni@S-1 with pre-edge (-150 to -30 eV relative to E0) and post-edge (+150 to +700 eV relative to E0) baselines before normalization. The E0 of Pt spectra is calibrated to 11535.0 e and the E0 of Ni spectra is calibrated to 8333.0 eV. The absorption strength is weaker for the four catalysts samples than Pt foil and Ni foil due to their low Pt and Ni loadings.

Samples	Pt wt%	Ni wt%	T <sub>CO100%</sub>
Pt@S-1	1.4%	0	90
Ni@S-1	0	0.6%	-
PtNi@S-1	1.5%	0.5%	30

Table S1 The ICP for PtNi@S-1, Ni@S-1 and Pt@S-1

Table S2 Physicochemical properties of related catalysts are measured by  $N_2$  sorption isotherms and CO-pulse adsorption.

Samples	$S_{BET}^{}/$ (m <sup>2</sup> /g)	$S_{ext}$ / (m <sup>2</sup> /g)	$V_{total}$ / (cm <sup>3</sup> /g)	V micro /(cm <sup>3</sup> /g)	V meso /(cm³/g)	Metal dispersion%
PtNi@S-1	356.14	56.68	0.2085	0.1471	0.0614	95
Ni@S-1	367.40	109.95	0.2120	0.1263	0.0857	89
Pt@S-1	366.91	79.78	0.3123	0.1410	0.0713	90

**S**<sub>BET</sub> : Calculated by BET method.

 $\mathbf{S}_{\text{ext}}$  : (external surface area) calculated using the t-plot method.

V<sub>total</sub>: Determined by BET method.

V<sub>micro</sub>: Determined by HK method.

V<sub>meso</sub>: Determined by BJH method

Samples		Activity	Activity	Ea	СО	Feed gas composition	Ref.
					conversion		
	°C	µmol/g <sub>metal</sub> /s	µmol/g <sub>cat</sub> /s	kJ/mol	%		
PtNi@S-1	30	5789	78.15	26.35	100	1%CO/20%O <sub>2</sub> /N <sub>2</sub>	this
							work
0.75Pt0.2Fe/ND@G	30	1719	16.33	22.72	100	1%CO/0.5%O <sub>2</sub> /N <sub>2</sub>	4
Pt/CoNiO <sub>x</sub>	30	-	-	-	100	1% CO/20%O <sub>2</sub> /He	5
Pt/Silicate-1	60	800	15.2	21	100	1%CO/20%O <sub>2</sub> /N <sub>2</sub>	6
Pd/FER	125	1555	28	57	100	-	7
Pt/CeO <sub>x</sub> /SiO <sub>2</sub>	250	1000	40	68	100	1% CO/4 %O <sub>2</sub> /He	8
Pt/SiO <sub>2</sub>	170	273.5	1.97	88.89	12	2.5%CO/5%O <sub>2</sub> /N <sub>2</sub>	9
PtNi@UiO-67	174	-	-	-	90	1% CO/20% O <sub>2</sub> /He	10
Pt <sub>3</sub> Ni	200	2222	22.22	-	45	1CO/2.5O <sub>2</sub> /He	11
CuPt nanocrystals	145	830.56	4.15	-	100	20%CO/12.5%O <sub>2</sub> /He	12
Pt–Ni/GS	175	-	-	-	100	1% CO/20% O <sub>2</sub> /N <sub>2</sub>	13
Pt/TiO <sub>2</sub>	120	3200	32	55.6	100	-	14
Pt-Na/HZSM-5	200	-	-	89.8	30	2.5%CO/5%O <sub>2</sub> /N <sub>2</sub>	15
2Cu/AlOOH	200	68.45	1.39	-	90	1% CO/20 %O <sub>2</sub> /N <sub>2</sub>	16
CoOx/Pt	125	-	-	-	6	-	17
Ni <sub>x</sub> CoyO <sub>4</sub>	239	-	8.9	-	100	-	18

Table S3 Comparison of the COOR performance of the PtNi@S-1 catalyst and other recently reported noble metal and 3d TM-based catalysts under thermal conditions.

Sample	Path	N	<i>R</i> / Å	$\sigma^2$ / Å	<b>R</b> -factor
Pt foil	Pt-Pt	12	2.76(1)	0.004	0.002
	Pt-O	1.2	1.96(1)	0.004	0.019
PtNi@S-1	Pt-Pt	1.8	2.73(1)	0.003	0.019
	Pt-Ni	0.6	2.34(1)	0.006	0.019
Ni@S-1	Ni-Ni1	8	2.68(1)	0.012	0.016
	Ni-O	3	2.04(1)	0.005	0.016
	Ni-Ni2	12	3.00(1)	0.010 <sup>s</sup>	0.016
Pt@S-1	Pt-Pt	1.6	2.01(1)	0.004	0.018
	Pt-O	1.2	2.67(1)	0.010	0.018

Table S4 Curve-fit Parameters for Pt L-edge and Ni K-edge EXAFS for PtNi@S-1, Ni@S-1 and Pt@S-1

 $S_0$  was fixes as 0.8.  $E_0$  was refined as a global parameter, returning a value of (8±1) eV. Data ranges:  $3 \le k \le 13$  Å-1,  $1.0 \le R \le 3.0$  Å for the PtNi@S-1 and Pt@S-1. The number of variable parameters is10 and 6, out of a total of 12.7 independent data points. Data ranges:  $1.5 \le k \le 12.5$  Å-1,  $1.0 \le R \le 3.0$  Å for the Ni@S-1. The number of variable parameters is 9, out of a total of 12.7 independent data points 14.01. R factor for the fits are 2 %, 1.9%, 1.6% and 1.8%. The Path for Pt-O, Pt-Pt, Pt-Ni, Ni-Ni are from the crystal structures.

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