

## Supporting Information

### One Pot Ligand Exchange Method for a Highly Stable Au- SBA- 15 Catalyst and its room temperature CO Oxidation

Yogita Soni<sup>a</sup>, I. Kavaya<sup>d</sup>, T. G. Ajithkumar<sup>c,d</sup>, C.P.Vinod<sup>a,b,c \*</sup>

<sup>a</sup>Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India

<sup>b</sup>CoE on Surface Science, CSIR-National Chemical Laboratory, Pune 411008, Maharashtra, India

<sup>c</sup>Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bhavan, 2 Rafi Marg, New Delhi 110001, Delhi, India

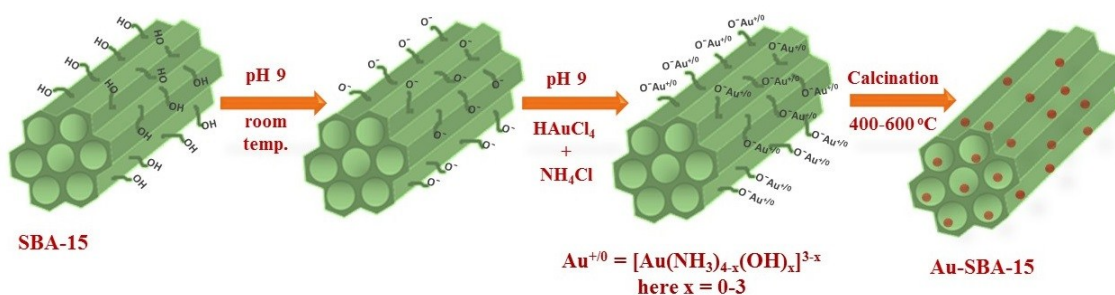
<sup>d</sup>Central NMR Facility and Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, Maharashtra, India

#### 1. Experimental Section

**1.1 Synthesis of SBA-15:** SBA-15 was synthesized according to the literature with some modifications<sup>1</sup>. 19.8 gm of P123 was dissolved in 135 mL water at room temperature. Subsequently 540 mL of 2M HCl was added followed by addition of 40 gm TEOS. A white precipitate was formed gradually. The solution was transferred to autoclave for hydrothermal treatment at 373K for 48 hr. Finally the SBA-15 was obtained by filtration, drying and calcination at 823 K.

**1.2 Synthesis of Gold supported Au/SBA-15:** Gold was supported on SBA-15 by modified deposition precipitation method using NH<sub>4</sub>Cl as the modifier. Typically, 500 mg of SBA-15 was dispersed in 50 mL water under sonication. To this solution required amount of NH<sub>4</sub>Cl was added. Then the pH of the solution was maintained at 9.45 using 0.1 M NaOH solution. To this solution required amount of gold precursor (for loading 2.8 wt% Au), HAuCl<sub>4</sub>.3H<sub>2</sub>O was added drop wise in 30 minutes while maintaining the pH at 9.45-9.5. The solution was stirred for another 1 hr at this pH. The as synthesized yellow colored Au/SBA-15 was obtained after centrifugation and drying and denoted as AS-x as syn. Here x refers to the millimoles of NH<sub>4</sub>Cl

used varied from 1 millimoles to 4 millimoles. The as synthesized Au/SBA-15 was calcined in air at 673 K for 4 hr at the ramp rate of 2° /min to finally get brown colored AS-x. Five different Au/SBA-15 catalysts have been synthesized and denoted as AS 1, AS 1.5, AS 2, AS 3 and AS 4. All the catalysts were stored in ambient conditions at room temperature without any precautions such as in dark and vacuum. The ICP analysis of the AS 4 catalyst showed Au metal loading 2.8 wt%.



Scheme 1: The schematic for the synthesis of Au supported SBA-15 catalyst

**Safety Note:** The mixing of gold chloride and ammonia solutions might lead to explosive gold compounds (fulminating gold). However, in this case we did not experience any such instances during the several batches of catalyst synthesis with  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}$ . In our procedure we use extremely small concentrations of (1-4 mmol) of  $\text{NH}_4\text{Cl}$  which certainly alleviate any risk of such explosive complex formation.

**1.3 Catalyst Characterization:** UV-visible analysis has been done by Shimadzu 2700 spectrophotometer with a dual beam source of He lamp and tungsten lamp as UV and visible light source. Liquid UV has been done using water as the reference. DRUV analysis has been done for powder samples using dual beam source equipped with a diffuse reflectance attachment by taking  $\text{BaSO}_4$  as the standard. Powder X-ray Diffraction has been recorded on Rigaku D MAX with a  $\text{Cu K}\alpha$  source of wavelength 1.54 Å with an operational voltage of 40 mV and 15 mA current.  $\text{N}_2$  adsorption /desorption analysis has been done using Autosorb 1C Quantachrome, USA. The sample was first degassed at 300 °C for 3 hr. After degassing the samples were cooled down to room temperature and analysis was done by adsorbing/ desorbing liquid  $\text{N}_2$  at different

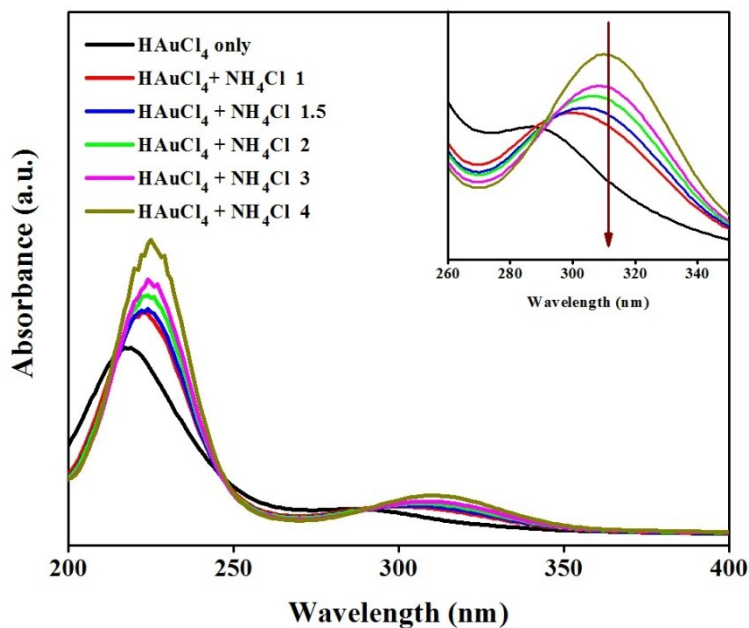
pressures. The surface area has been calculated by BET model. Pore size distribution has been calculated using BJH method. TEM analysis has been carried out by TECHNAI FEI instrument working at voltage of 200kV with LaB<sub>6</sub> as the filament. The samples for TEM analysis were prepared in ethanol and dried completely before analysis. Raman analysis was done by Renishaw InVia microscope with a Laser wavelength of 532 nm in the back scattering geometry. The liquid samples were drop casted on glass slide and dried under vacuum at room temperature.

The <sup>15</sup>N CPMAS NMR spectra were collected on a Bruker Avance HD 700 MHz spectrometer in a 4 mm double resonance probe with Larmor frequency of 70.94 MHz for <sup>15</sup>N. The data were collected using a cross polarisation time of 1ms and a recycle delay of 4s. The single pulse <sup>1</sup>H MAS experiments were done at Bruker AV NEO 500MHz equipped with a 2.5mm trigamma probe at a sample rotation frequency of 32 kHz. In the MAS NMR, a 90° pulse duration of 1.9µs and a recycle delay of 4s was employed. Glycine and adamantane were used as a chemical shift secondary references for <sup>15</sup>N and <sup>1</sup>H respectively. <sup>15</sup>N labelled ammonium chloride (<sup>15</sup>NH<sub>4</sub>Cl) was used for the synthesis of modified Au-SBA-15 and SBA-15 samples. Synthesis procedure was same as explained in experimental section.

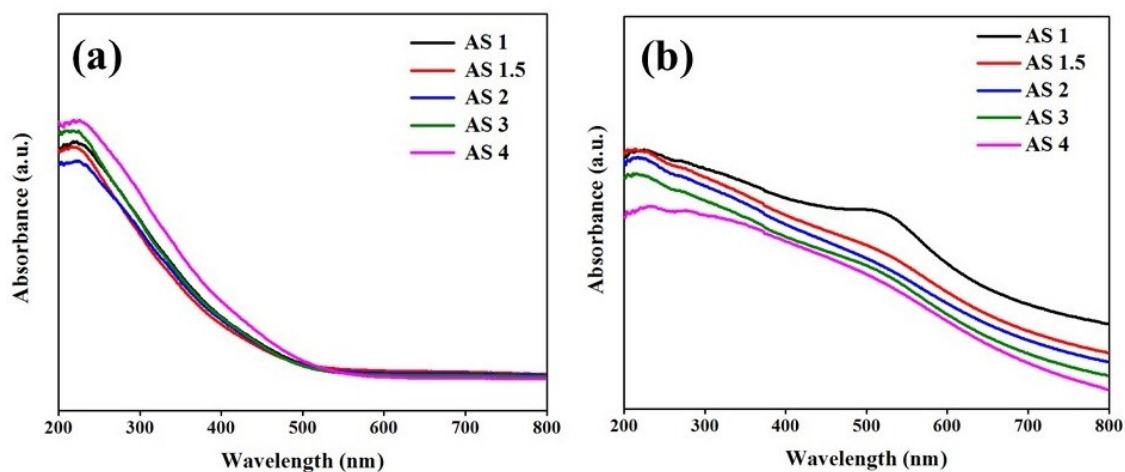
XPS measurements were carried out using Thermo Kalpha+ spectrometer using micro focused and monochromated Al Kα radiation with energy 1486.6 eV. The pass energy for spectral acquisition was kept at 50 eV for individual core-levels. The electron flood gun was utilized for providing charge compensation during data acquisition. The peak fitting of the individual core-levels were done using XPSpeak 41 software with a Shirley type background. The samples were prepared by drop casting the NH<sub>4</sub>Cl modified Au precursor (unsupported) on silicon wafer and dried under ambient conditions.

**1.4 Catalytic Test: CO oxidation.** The synthesized AS-x catalysts were tested for CO oxidation without any pretreatment. The catalyst tests were done in a fixed bed reactor of diameter 14mm at atmospheric pressure. Typically, 50 mg of pelletized the catalyst was loaded in a silica reactor supported by quartz wool. The reactor was placed in a tubular furnace with a uniform heating zone of 4 cm furnished with temperature controller radix 6400. A K-type thermocouple was placed on the thermowell was used to measure the temperature of catalyst bed. The flow rate of the reaction gases was 25 mL min<sup>-1</sup> CO: O<sub>2</sub>: N<sub>2</sub> = 1:5:19) with a GHSV of 30,000 cm<sup>3</sup> (g<sub>cat</sub>.h)<sup>-1</sup>. The gas flow of CO, O<sub>2</sub> and N<sub>2</sub> was

controlled by Brooks Mass flow Controllers. The gas exiting the reactor was analyzed by Nucon 5700 GC equipped with a molecular sieve column with thermal conductivity detector at isothermal conditions. The % conversion of CO was calculated using the formula:  $[(CO_{in}-CO_{out})/CO_{in}]*100$ .

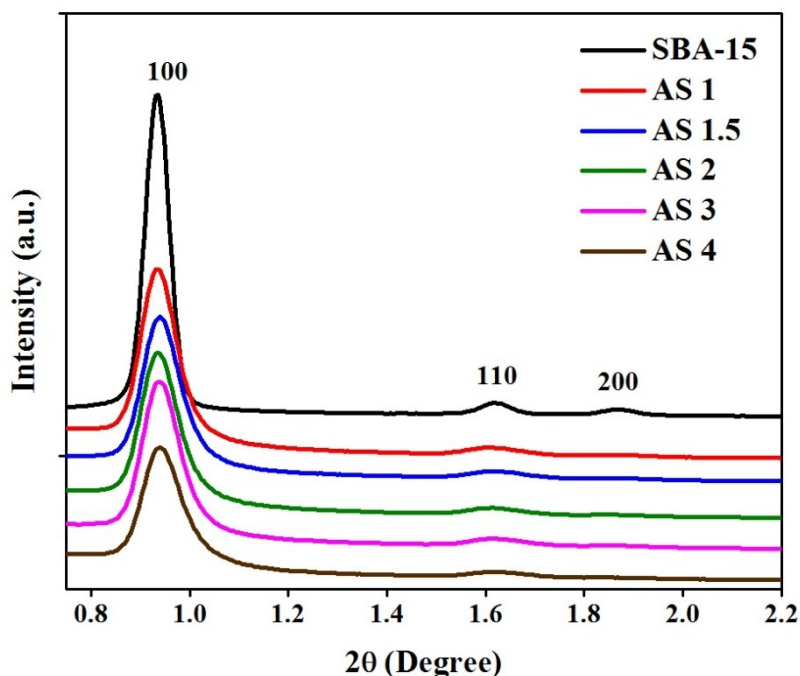


**Fig. S1** UV-Visible spectrum of Au precursor solution with different millimoles of NH<sub>4</sub>Cl



**Fig. S2** DRUV spectra of AS x (a) as synthesized and (b) calcined catalysts.

Electronic environment of the gold in the precursor with different millimoles of  $\text{NH}_4\text{Cl}$  is followed by UV-Vis spectroscopy. The two UV bands at 217 and 290 nm (Fig. S1) assigned to the ligand to metal charge transfer (LMCT) between  $\text{Au}^{3+}$  and  $\text{Cl}^-$  ions<sup>[2]</sup> show a shift towards the higher wavelength after the addition of  $\text{NH}_4\text{Cl}$ . But the shift is more prominent for 290 nm band (shown in the inset of Fig. S1) and increases with an increase in the amount of  $\text{NH}_4\text{Cl}$  from 1 mm to 4 mm which is attributed to the electrostatic interaction between  $\text{NH}_4^+$  ions with gold complex.<sup>2</sup> DRUV-visible spectra in the range 500-600 nm for AS x is featureless for the synthesized sample (Fig. S2(a)) and shows SPR band at 510 nm after calcination due to the generation of metallic Au NPs (Fig. S2(b)). The samples with increased  $\text{NH}_4\text{Cl}$  show a broad SPR band with very less intensity and is usually observed for Au NPs of  $< 3$  nm.<sup>3</sup> Decrease in the intensity of SPR band of the gold with increasing  $\text{NH}_4\text{Cl}$  amount shows that size of the Au NPs decreases when amount of  $\text{NH}_4\text{Cl}$  increases from 1 mm to 4 mm.



**Fig. S3** Small angle XRD of AS x catalysts compared with pristine SBA-15.

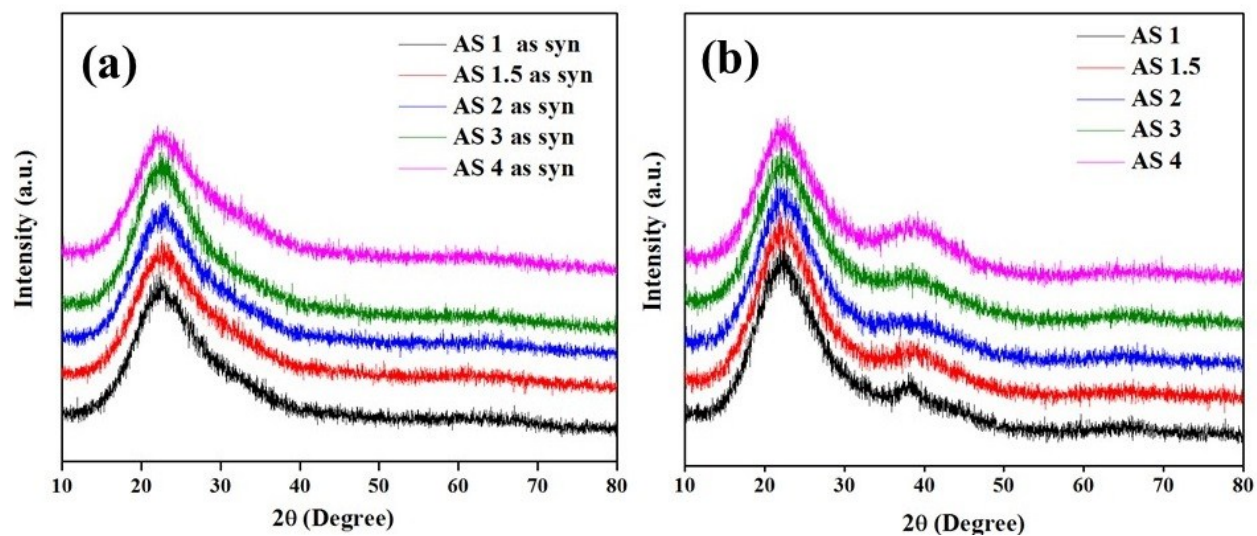


Fig. S4 Wide angle XRD of AS x catalysts (a) as synthesized and (b) calcined at 400°C.

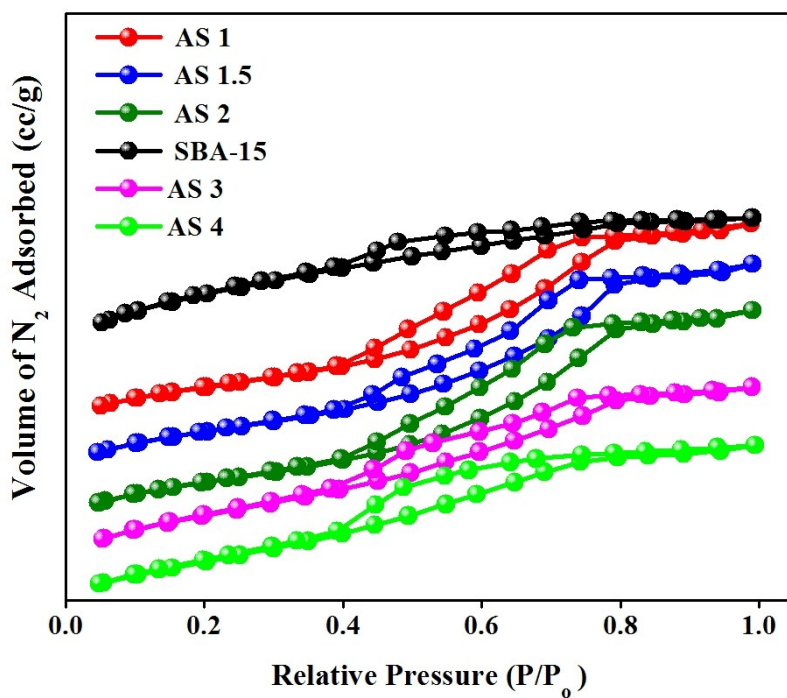


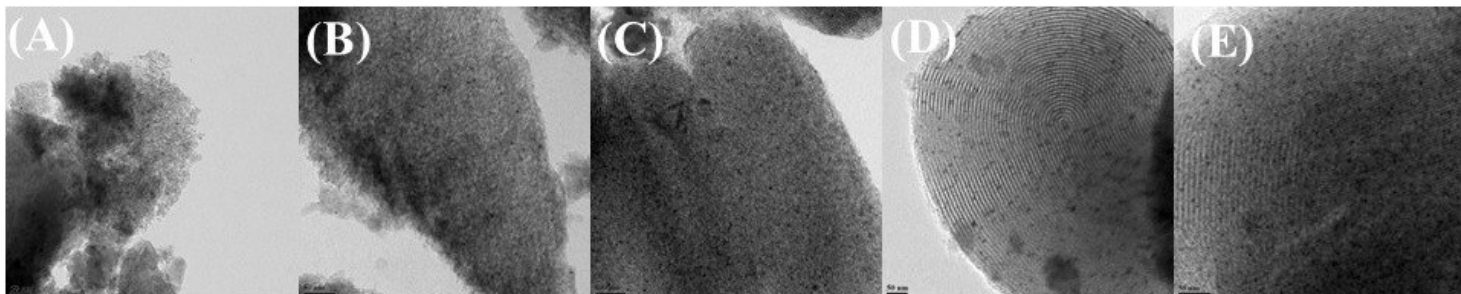
Fig. S5 Comparative N<sub>2</sub> Adsorption isotherms of SBA-15 and AS x catalysts

Sample Name	Surface Area (m <sup>2</sup> /g)	Pore diameter (nm)	Pore volume (cc/g)
SBA-15	575	5.6	0.492
AS 1	401	4.2	0.468
AS 1.5	350	4.8	0.486
AS 2	345	4.8	0.412
AS 3	330	3.7	0.427
AS 4	370	3.3	0.386

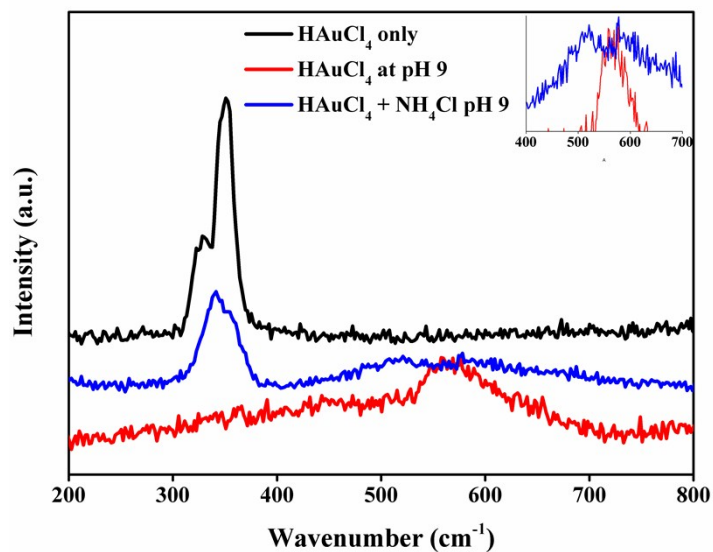
**Table S1** Textural properties of SBA-15 and Au supported SBA-15

XRD and BET surface area measurements show characteristic features of mesoporous materials. Three diffraction peaks at 0.93 °, 1.63 ° and 1.86° corresponding to (100), (110) and (200) in small angle XRD of AS x (Fig. S3) calcined catalysts compared with pristine SBA-15 sample confirms the ordered 2D hexagonal structure of SBA-15 with a space group of *p6mm*.<sup>1</sup> The intensity of (100) reflection decreases after supporting Au NPs indicating successful deposition of Au in the channels of SBA-15. No reflection from metallic Au at 38.3° can be seen in any of the AS samples which indicates that as synthesized AS samples consists mainly of oxidized gold (Fig. S4(a)). The metal feature appears after calcination at 400 °C indicating the reduction of Au ions to Au<sup>0</sup> under calcination (Fig. S4(b)). FWHM of peak at 38.3° in AS samples increases with an increase in NH<sub>4</sub>Cl amount (from 1.8 in AS1 to 4.3 for AS 4) hence supporting our claim that NH<sub>4</sub>Cl helps in minimizing the particle size of gold NPs in the final catalyst. The BET surface area measurements done by the N<sub>2</sub> adsorption desorption isotherms of pristine SBA-15 and other Au NPs supported samples show type IV hysteresis (Fig. S5) corresponding to the filling of mesopores present in all samples.<sup>4</sup> The physicochemical characteristics of the materials obtained after surface area analysis are listed in Table S1. The pore size, pore volume and surface area are

found to decrease as the amount of  $\text{NH}_4\text{Cl}$  increases from AS 1 to AS 4 which is a manifestation of successful loading of Au inside the pore channels.



**Fig S6.** TEM images of AS (A) 1 (B) 1.5 (C) 2 (D) 3 and (E) 4 catalysts. Scale Bar: 50nm (AS 1 and 1.5 samples). AS1 and AS 1.5 show some partial destruction in the hexagonal array of SBA-15 which is due to deposition of large Au NPs in SBA-15.



**Fig S7:** Raman spectra of gold complex in different conditions. ( $\text{NH}_4\text{Cl}$ : 4 millimoles)



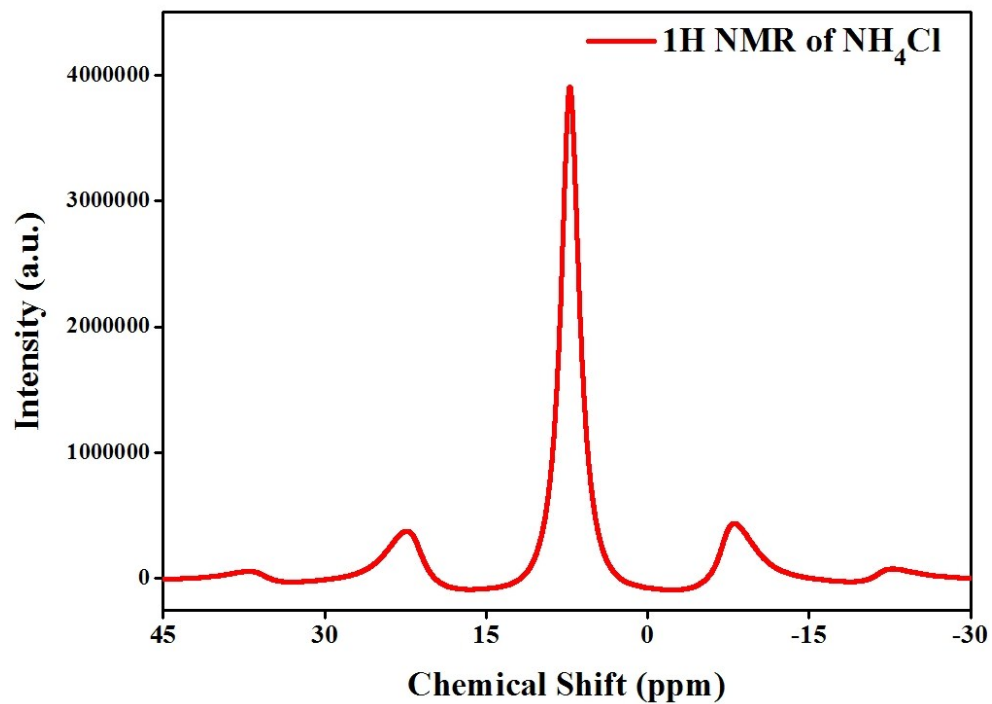


Fig. S8  $^1\text{H}$  Solid state NMR of pure  $\text{NH}_4\text{Cl}$

Sample Name	$\text{Au}^{+1} 4f_{7/2}$	$\text{Au}^{+3} 4f_{7/2}$	$\text{Au}^{+1} 4f_{5/2}$	$\text{Au}^{+3} 4f_{5/2}$
$\text{HAuCl}_4$	85.1	87.7	89.2	91.2
$\text{HAuCl}_4 + \text{NaOH}$	84.4	86.8	88.4	90.4
$\text{HAuCl}_4 + \text{NH}_4\text{Cl}$ at pH 7	84.8	87.3	88.9	90.9
$\text{HAuCl}_4 + \text{NH}_4\text{Cl}$ at pH 9	84.8	87.3	88.9	90.9
$\text{HAuCl}_4 + \text{NH}_4\text{Cl}$	85.0	87.6	88.9	91.0

Table S2. XPS binding energy values of Au 4f core level in different conditions

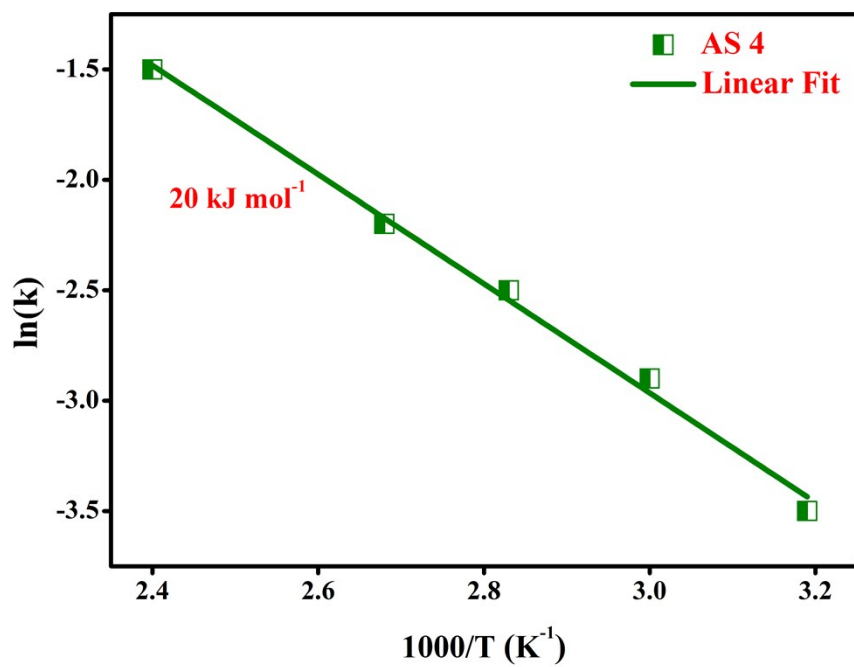


Fig. S9. Arrhenius plot of AS 4 catalyst for activation energy calculation.

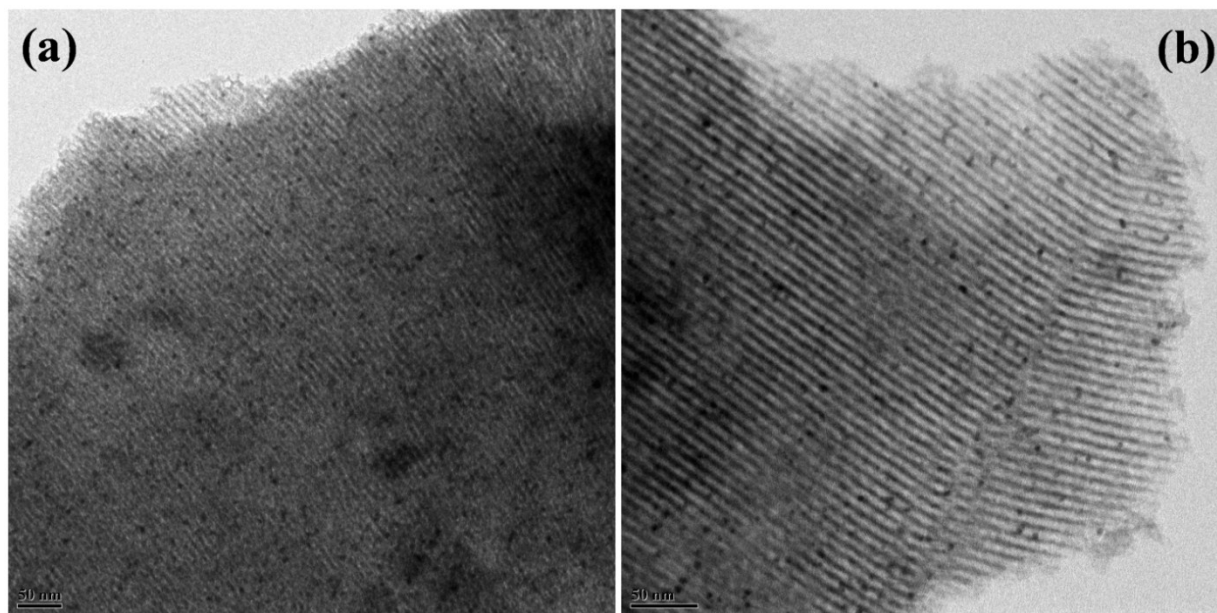
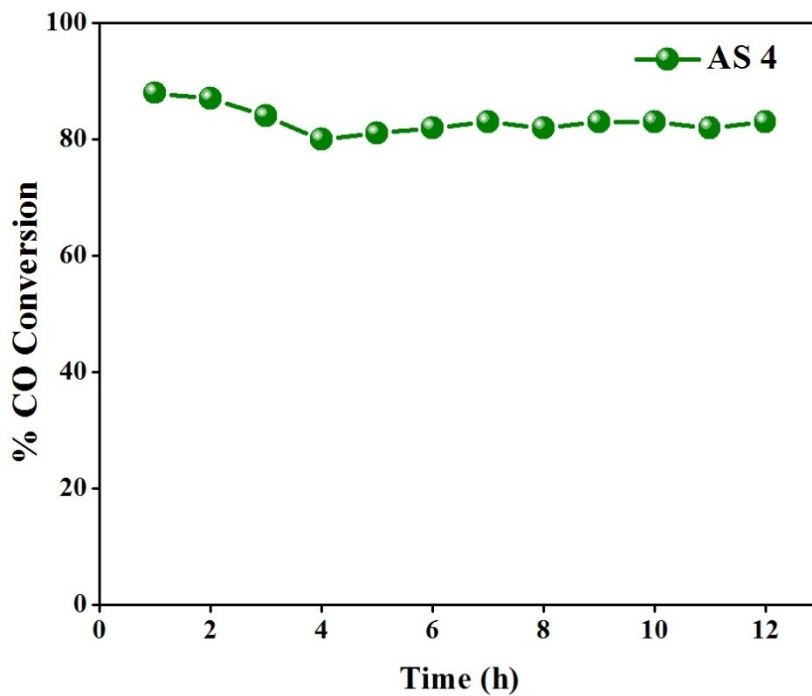
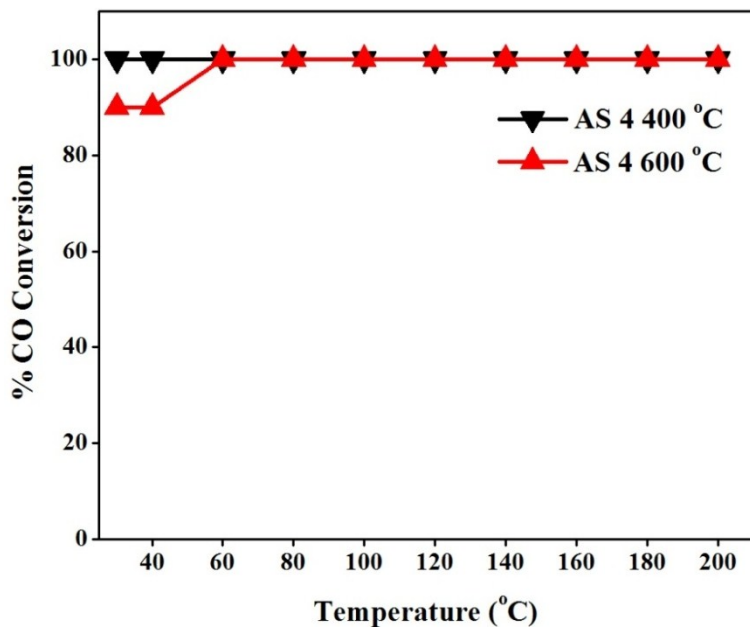


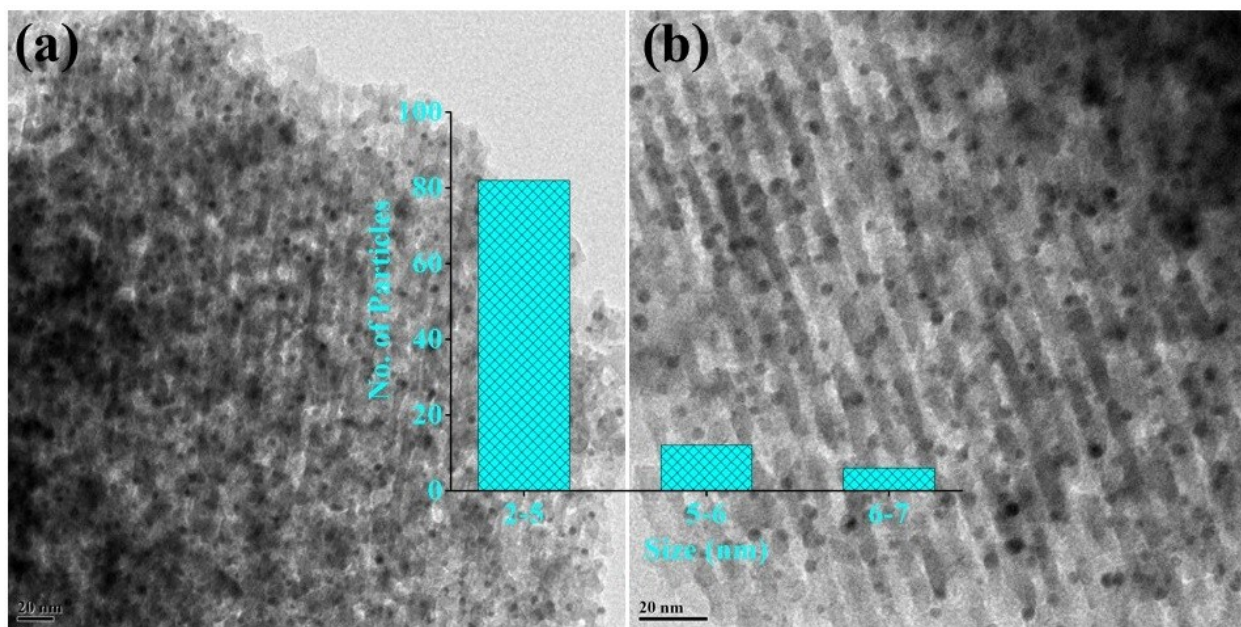
Fig. S10 TEM images of AS 4 spent catalyst after 48 hr time on stream. Scale bar: 50 nm



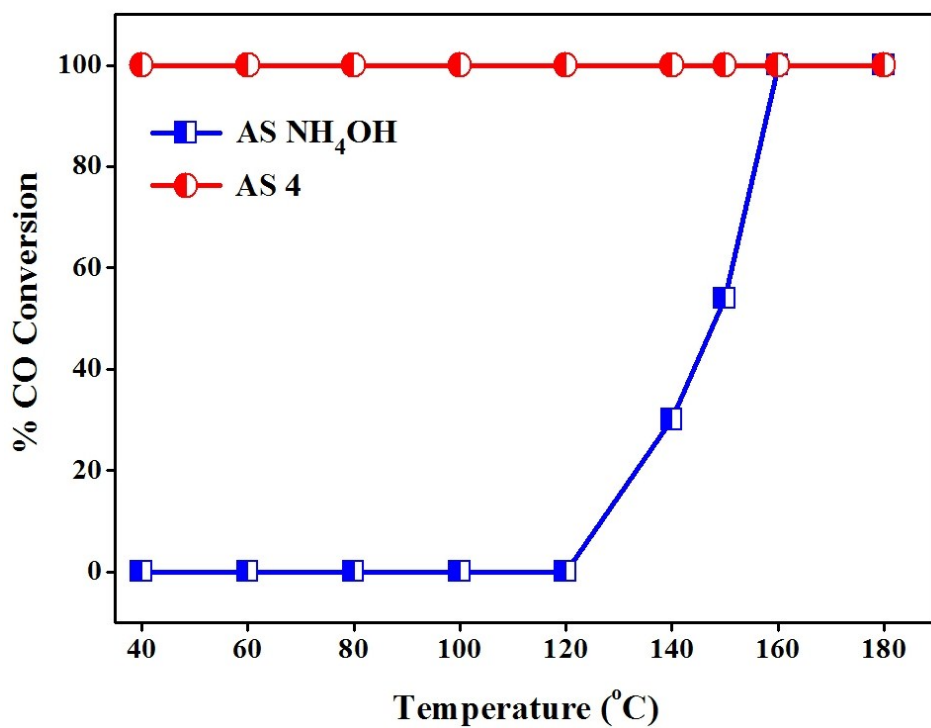
**Fig. S11** CO Oxidation activity of AS 4 catalyst at room temperature with double GHSV (60,000 mL(g<sub>cat</sub>.h)<sup>-1</sup>)



**Fig. S12** Comparison of CO oxidation activity of AS 4 catalyst calcined at 400 °C and 600 °C.



**Fig. S13** TEM images of AS 4 calcined at 600 °C shows negligible increase in the Au NPs size and particles are still well dispersed in the SBA-15 channels.



**Fig. S14** Activity comparison of AS 4 catalyst with AS NH<sub>4</sub>OH catalyst (synthesized using NH<sub>4</sub>OH)

<b>Catalyst</b>	<b>D<sub>Au</sub>(wt%)</b>	<b>Synthesis method</b>	<b>GHSV ml(g*<sup>h</sup>)<sup>-1</sup></b>	<b>CO: O<sub>2</sub></b>	<b>TOF/s<sup>-1</sup> (T°C: Conversion%)</b>	<b>Ref.</b>
<b>AS-4</b>	2-3 nm (2.8)	Modified DP	1,50,000	1:5	0.071 (30°C: <b>16%</b> ) Specific rate: 1.32 mol <sub>CO</sub> (g <sub>Au</sub> *h) <sup>-1</sup> at 30°, 16% conversion	<b>This Work</b>
<b>Au/SiO<sub>2</sub></b>	6 nm (7)	CVD*	20,000	1%CO/ air	0.02 (0°C: <b>100%</b> )	<b>5</b>
<b>Au/SBA-15</b>	3 nm (9)	Au(en) <sub>2</sub> Cl <sub>3</sub>	44,400	1%CO/ air	0.45 (-20 °C: <b>50%</b> )	<b>6</b>
<b>Au/SBA-15</b>	2-3 nm	Using silanes (MPTMS)*	66,000	1:1	0.11 (80 °C: <b>28%</b> )	<b>7</b>
<b>Au/SBA-15</b>	4.5 nm(5)	Silanes modification	20,000	1%CO/ air	0.002 (90°C: <b>33%</b> )	<b>8</b>
<b>Au/SiO<sub>2</sub></b>	2 nm (2)	Silane modification	-		Specific rate: 0.48 mol <sub>CO</sub> (g <sub>Au</sub> *h) <sup>-1</sup> at 30°, 75% conversion	<b>9</b>
<b>Au/SiO<sub>2</sub></b>	3 nm(2.5)	Au(en) <sub>2</sub> Cl <sub>3</sub>	44,400	1%CO/ air	Specific rate: 0.60 mol <sub>CO</sub> (g <sub>Au</sub> *h) <sup>-1</sup> at 0°, 82% conversion	<b>10</b>
<b>Au/SBA-15</b>	2.5 nm (2.5)	Modification with ammonia	-	1:1	Specific rate: 0.014 mol <sub>CO</sub> (g <sub>Au</sub> *h) <sup>-1</sup> at 40°, 82% conversion	<b>11</b>

<b>Au/SiO<sub>2</sub></b>	2-3 nm (6)	PVD*	1,80,000	1:8	0.019 (25°C)	<b>12</b>
<b>Au/SBA-15</b>	2-3 nm(3.8)	Au(en) <sub>2</sub> Cl <sub>3</sub>	1,00,000	1:1	0.098 (25°C: <b>98%</b> ) Specific rate: 1.15 mol <sub>CO</sub> (g <sub>Au</sub> *h) <sup>-1</sup> at 25°, 98% conversion	<b>13</b>

**Table S3** Comparison of activity of Au/SiO<sub>2</sub> based catalysts

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