Supporting Information

Remarkable Enhancement of Fe-V-O$_x$ Composite Metal Oxides to Gold Catalysts for CO Oxidation in the Simulated Atmosphere of CO$_2$ Laser

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† *Electronic Supplementary Information (ESI) available: the characterization data of XRD, HAADF-STEM, XANES and Raman spectra. See DOI: 10.1039/b000000x/*

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1. Catalyst preparation

1.1 Preparation of FeO_x and VO_x modified Al_2O_3 composites

FeO_x and VO_x modified Al_2O_3 composites with 1:1 atomic ratio of Fe:V were prepared by an incipient wetness impregnation. Typically, at room temperature, 10 g of the commercially available spherical support γ-Al_2O_3 (Alumina Corporation of China, 20 - 40 mesh, ~157 m^2/g) was added to the aqueous solutions of $Fe(NO_3)_3$ (0.08 mol/L, 15 mL in ultra-pure water; Sinopharm Chemical Reagent Co., Ltd.). After sufficient mixing and aging for 2 h, the sample was dried at 120 °C for 4 h, and then added to the aqueous solution (15 mL) of NH_4VO_3 (0.08 mol/L in ultra-pure water, Tianjin Boding Chemical Co., Ltd.). Finally, the sample was dried at 120 °C for 4 h and then calcined at 600 or 800 °C for 4 h. The obtained FeO_x and VO_x modified Al_2O_3 composites were denoted as Fe-V-O_x/Al_2O_3.

1.2 Preparation of supported Au catalysts

The γ-Al_2O_3, Fe-V-O_x/Al_2O_3 supported Au catalysts were all prepared by deposition-precipitation method: typically, an aqueous solution of $HAuCl_4$ (0.0971 mol/L in ultra-pure water, Sinopharm Chemical Reagent Co., Ltd.) was taken into a beaker, and its pH value was adjusted to about 7 by dropwise addition of aqueous solution of 1 mol/L KOH. The support (γ-Al_2O_3, or Fe-V-O_x/Al_2O_3) with a mass of 1 g was added into the solution and mixed thoroughly. After completely being washed with ammonia solution and ultra-pure water to remove the chloride residue, the sample was dried in air at 60 °C for 12 h. The obtained samples were denoted as Au/Al_2O_3 and Au/ Fe-V-O_x/Al_2O_3, respectively. Prior to the reaction tests, the catalyst samples were further in-situ reduced with H_2 at 300 °C for 60 min.

1.3 Activity test

The CO oxidation process in the simulated atmosphere of CO_2 laser was examined in a continuous flow fixed-bed reactor under atmospheric pressure. The catalyst (10 mg) diluted in 10 mg Al_2O_3 was loaded into a U-shape quartz reactor, the feed gas containing 60 vol.% CO_2, 1.0 vol.% CO, 0.5 vol.% O_2, 0.5 vol.% H_2O and balanced with N_2 was passed through the reactor at a flow rate of 100 mL/min, corresponding to a total space velocity of 60, 000 mL h^{-1} g_{cat}^{-1}. Before the test, the samples were in-situ reduced with H_2 at 300°C for 1 h.

The reactant gas and effluent gas from the reactor were first passed through an ice-bath unit to let the feed gas contain a little amount of water vapor, and then analyzed on line with an Agilent 7820A gas chromatograph using helium as carrier gas.

The specific reaction rates of CO oxidation in the simulated atmosphere of CO_2 laser were measured at different temperatures in the feed gas containing 1 vol.% CO, 0.5 vol.% O_2, 60 vol.%CO_2, 0.5 vol.% H_2O (balanced with N_2), with a weight hourly space velocity (WHSV) of 849, 000 mL g_{cat}^{-1} h^{-1}, and the conversions of CO were controlled below 15 %. Towards this goal, 10 - 50 mg (20 - 40 mesh) of the sample was diluted with 250 mg γ-Al_2O_3 (20 - 40 mesh). For each run, the conversions of CO during the first 2 h were averaged and used for calculations of the specific reaction rates. The specific formation rate of CO_2 were also tested at 200 ^{o}C as mentioned above in the feed gas containing 97 vol.% CO in N_2, with a WHSV of 10, 133 mL g_{cat}^{-1} h^{-1}, where the feed gas contain no or very little O_2.

In addition, the catalyst's stability for CO oxidation in the simulated atmosphere of CO_2 laser were measured at 220 ^{o}C in the feed gas containing 1 vol.% CO, 0.5 vol.% O_2, 60 vol.%CO_2, 0.5 vol.% H_2O (balanced with N_2), with a WHSV of 154, 200 mL g_{cat}^{-1} h^{-1}.

1.4 Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer, using Cu Kα monochromatized radiation (λ = 0.1541 nm) at a scan speed of 5° min^{-1}.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a Titan G2 80-200 with Chemi STEM. High-resolution TEM images (HRTEM) were taken on a Tecnai G2 F30 Field Emission Gun Transmission Electron Microscope.

The X-ray absorption spectra (XAS) were measured at the BL14B2 in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI), Japan. The storage ring energy is 8 GeV with a beam current of 99.5 mA under a top-up injection mode. The samples were reduced in H_2 at 300 ^{o}C for 1 h. The samples were ground with boron nitride and packed into pellets. Au L_3-edge X-ray absorption near edge structure (XANES) spectra were measured using Si(311) double crystal monochromator in transmission mode. Ionization chambers were used to measure the intensity of the incident and transmitted X-rays, and the quick scan technique was used. The data analysis package (Athena) [1] was used for the normalization by edge-jump.

Temperature-programmed desorption of oxygen (O_2-TPD) experiments were evaluated on an automatic Chemisorption analyzer ChemCAA-TP5080. Prior to the O_2-TPD experiment, 100 mg of the sample was loaded into a U-shape quartz reactor and thermally treated in air at 300 ^{o}C for 30 min to remove adsorbed carbonates and hydrates. Then, after cooling to room temperature, the flowing gas was switched to pure He gas with a flow rate of 30 mL min^{-1}, and the catalyst was heated to 700 ^{o}C at a ramping rate of 10 ^{o}C min^{-1}.

2 References

[1] B. Ravel, M. Newville, *J. Synchrotron Radiat.* 2005, **12**, 537.

Supporting figures

Tab. S1 Physical properties of various supported Au catalysts

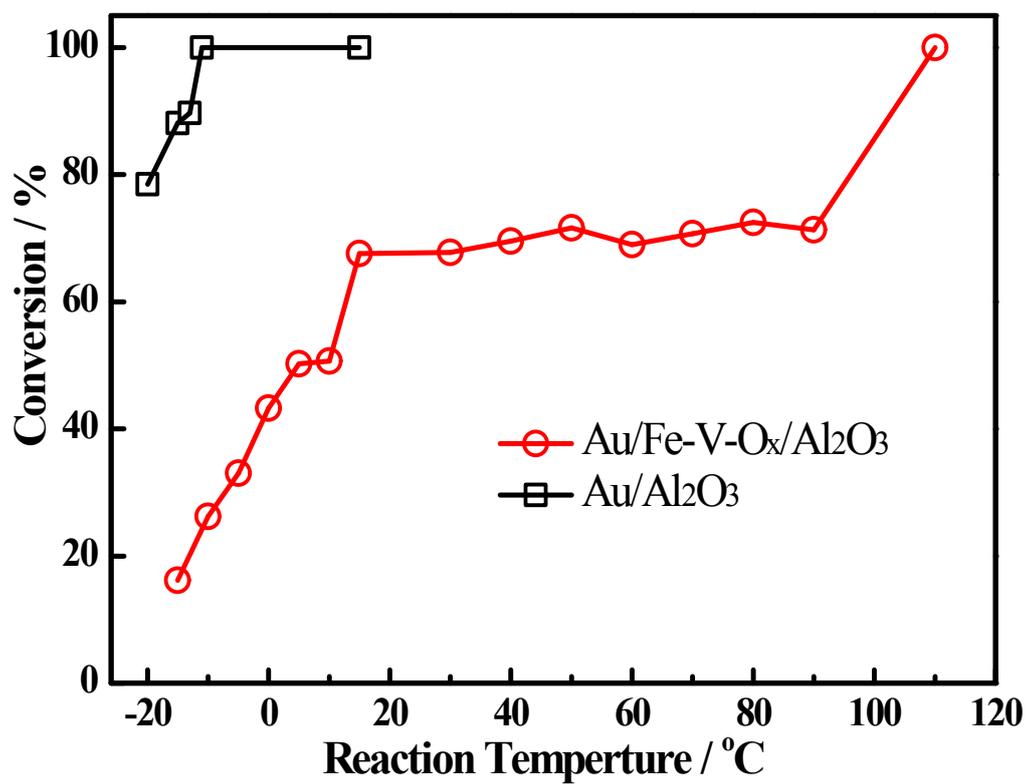| Catalyst	Au nominal loading (wt %)	Au actual loading (wt %)	BET surface area ($m^2 g^{-1}$)
Au/Al$_2$O$_3$	1.0	0.77	152
Au/Fe-V-O$_x$/Al$_2$O$_3$	1.0	0.23	151

Fig. S1 The activities of Au/Fe-V-O$_x$/Al$_2$O$_3$ in the reaction of CO oxidation
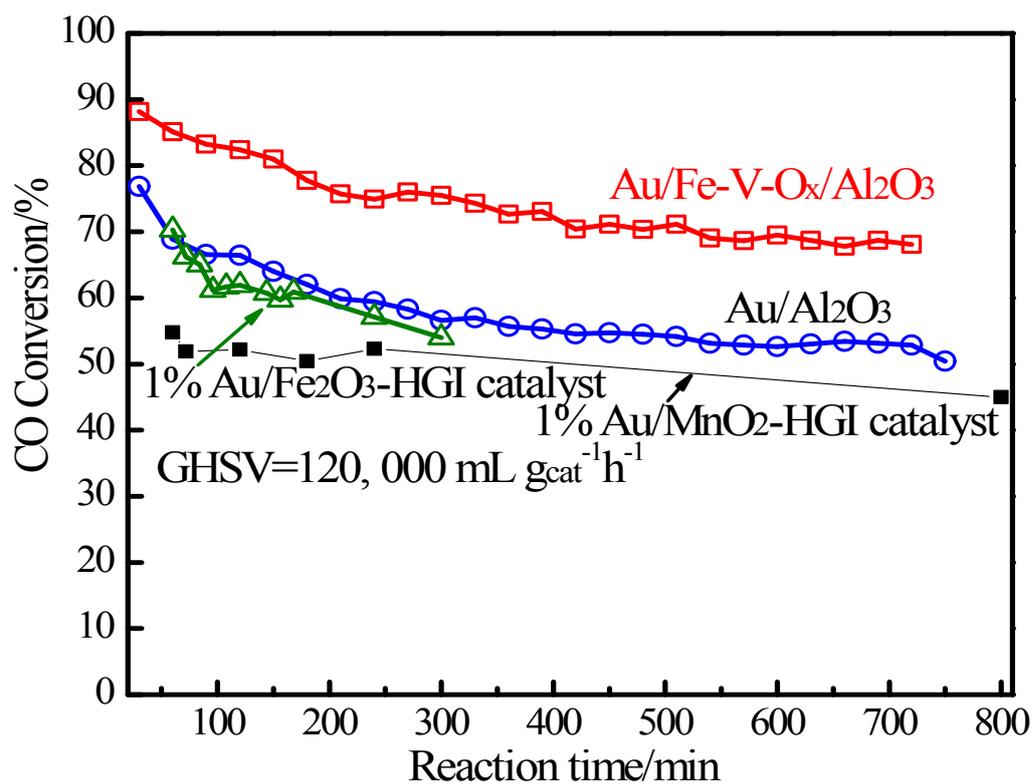Reaction conditions: 1 vol.% CO + air. WHSV: 60, 000 mL g$_{cat}^{-1}$ h^{-1}

Fig. S2 The stabilities of Au/Fe-V-O$_x$/Al$_2$O$_3$ in the simulated atmospheres of CO$_2$ laser

Reaction conditions: 60 vol.% CO$_2$ + 1 vol.% CO + 0.5 vol.% O$_2$ + 0.5 vol.% H$_2$O and balanced with N$_2$. WHSV: 154, 200 mL g$_{cat}$$^{-1}$ h^{-1}, reaction temperature: 220 ^{o}C.

Note: The 1%Au/Fe$_2$O$_3$-HGI catalyst was provided by Haruta Gold Incorporation and

prepared by M. Haruta's laboratory.
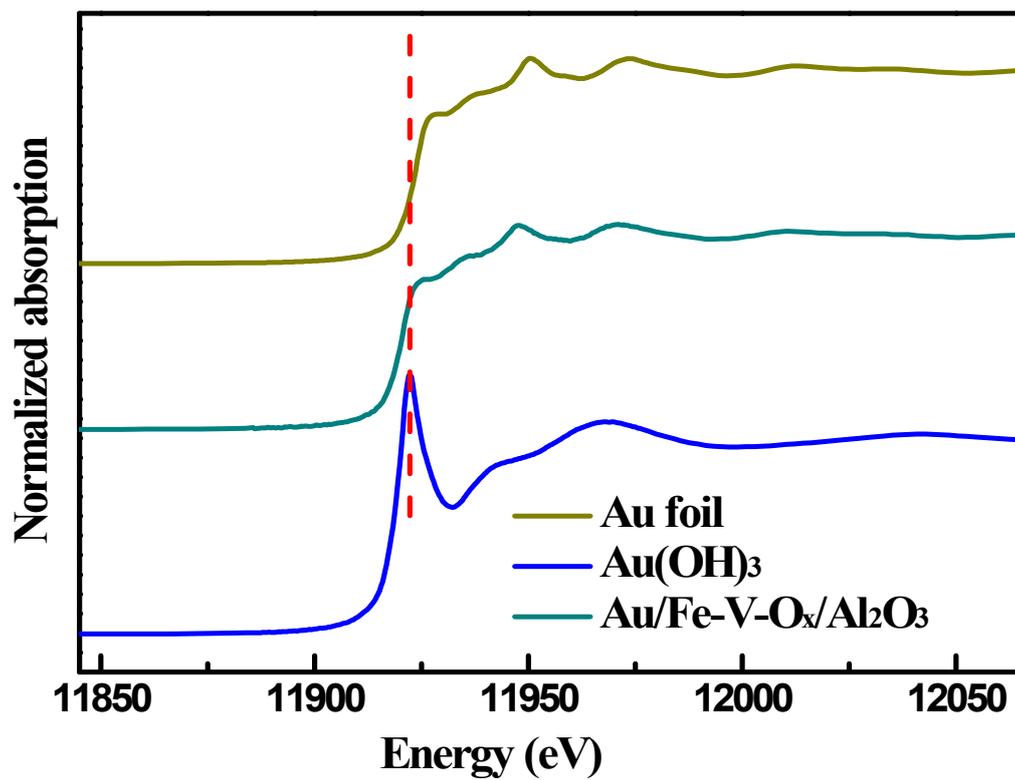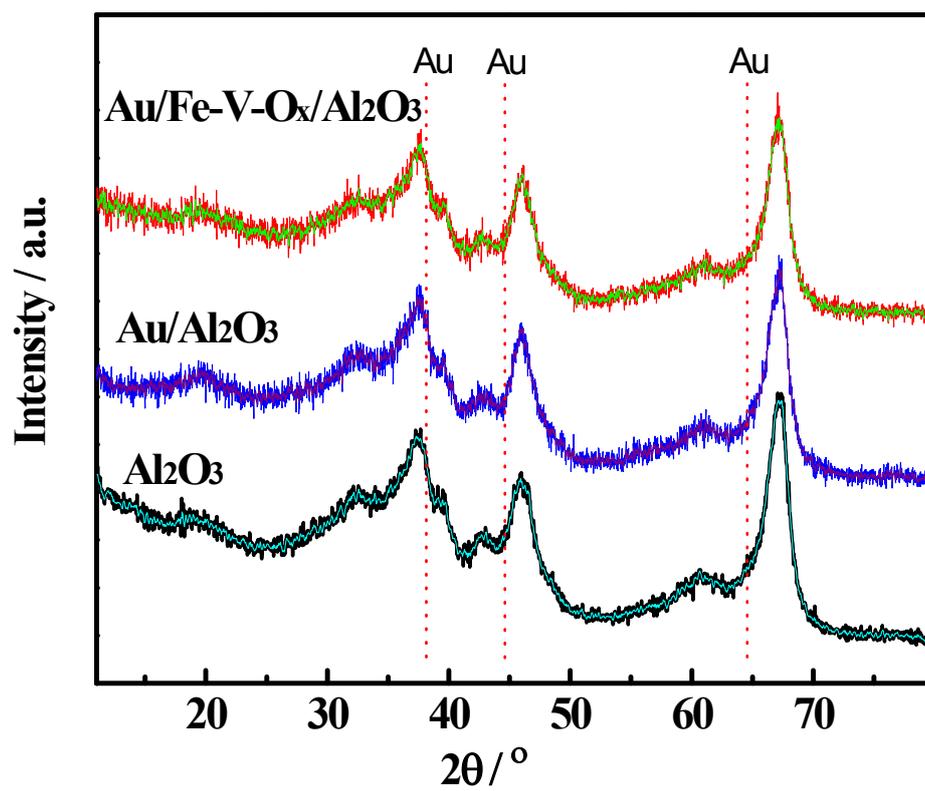
Fig. S3 The normalized Au L$_3$-edge XANES spectra for Au/Fe-V-O$_x$/Al$_2$O$_3$ catalysts

Fig. S4 XRD diffraction patterns of Al$_2$O$_3$, Au/Al$_2$O$_3$ and Au/Fe-V-O$_x$/Al$_2$O$_3$ samples
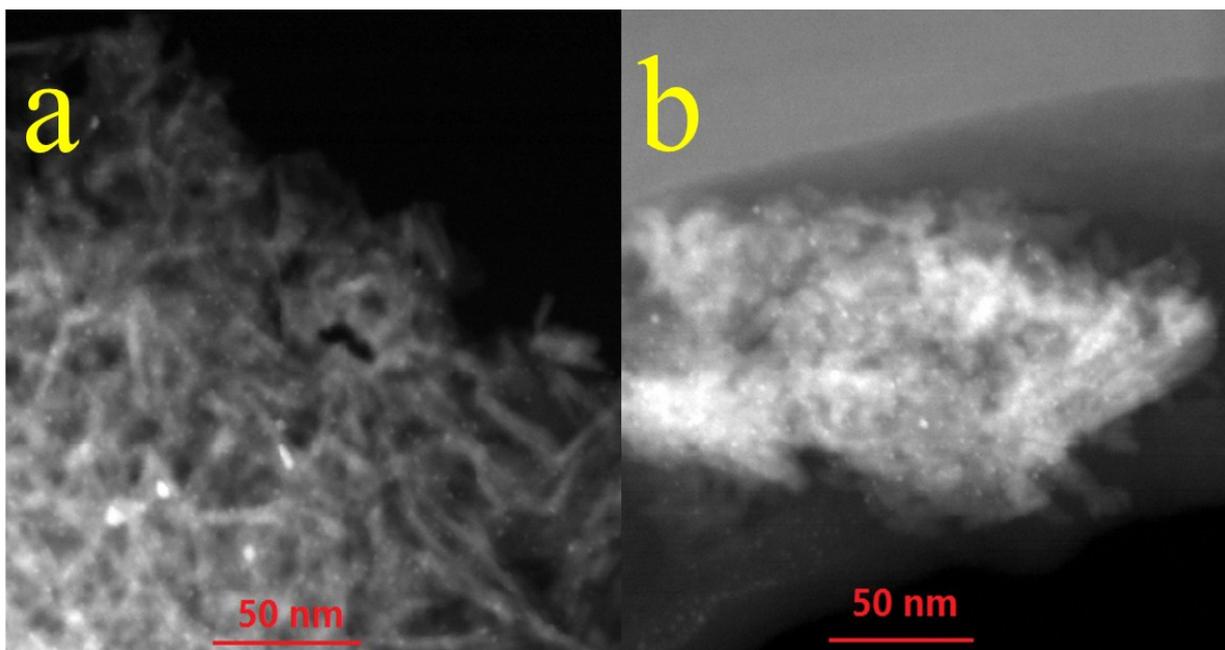
Fig. S5 The HAADF-STEM images of Au/Al₂O₃ catalysts
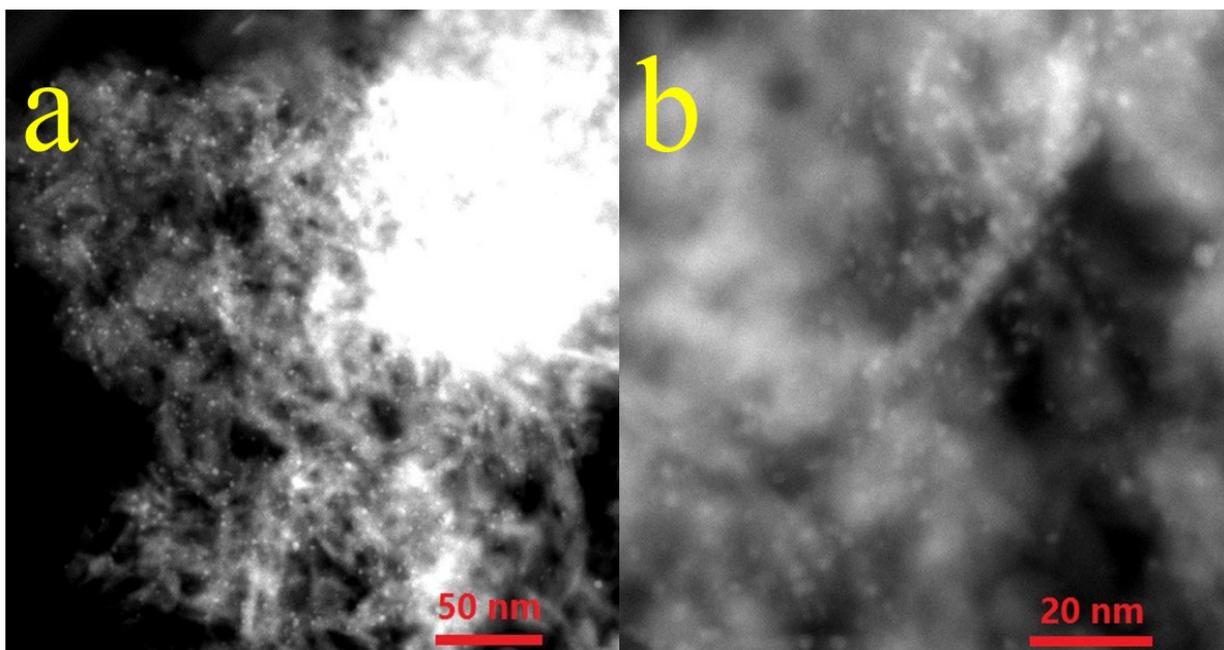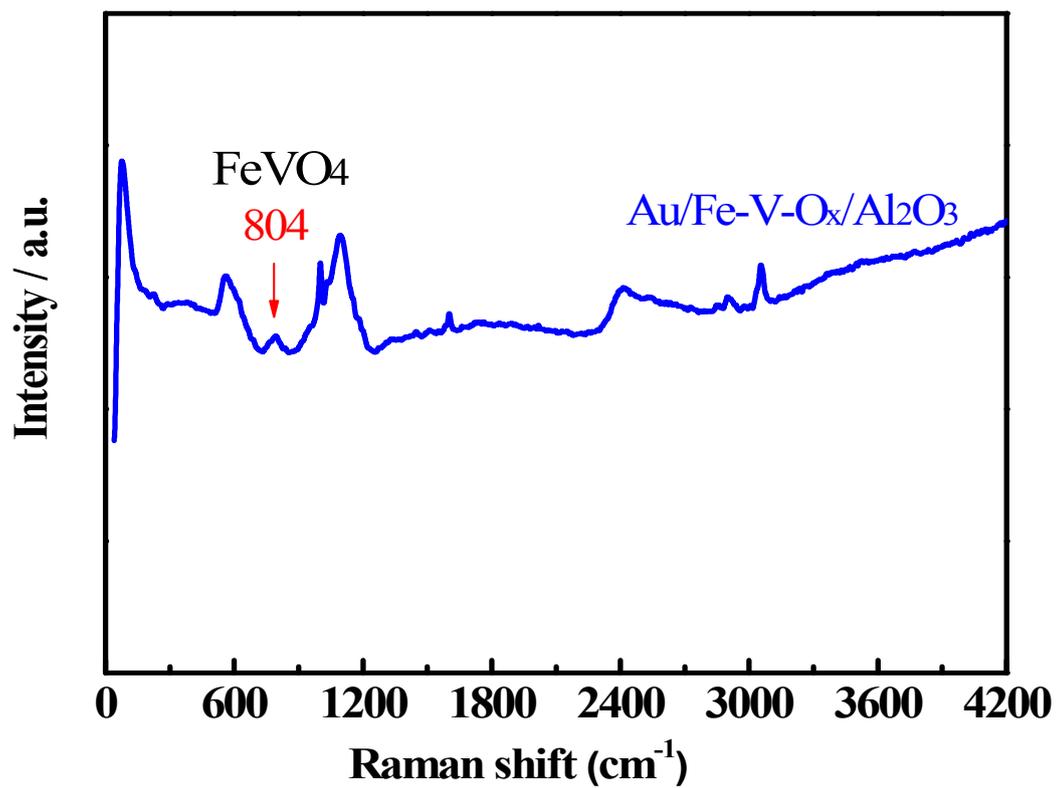
Fig. S6 The HAADF-STEM images of Au/Fe-V-O$_x$/Al$_2$O$_3$ catalysts

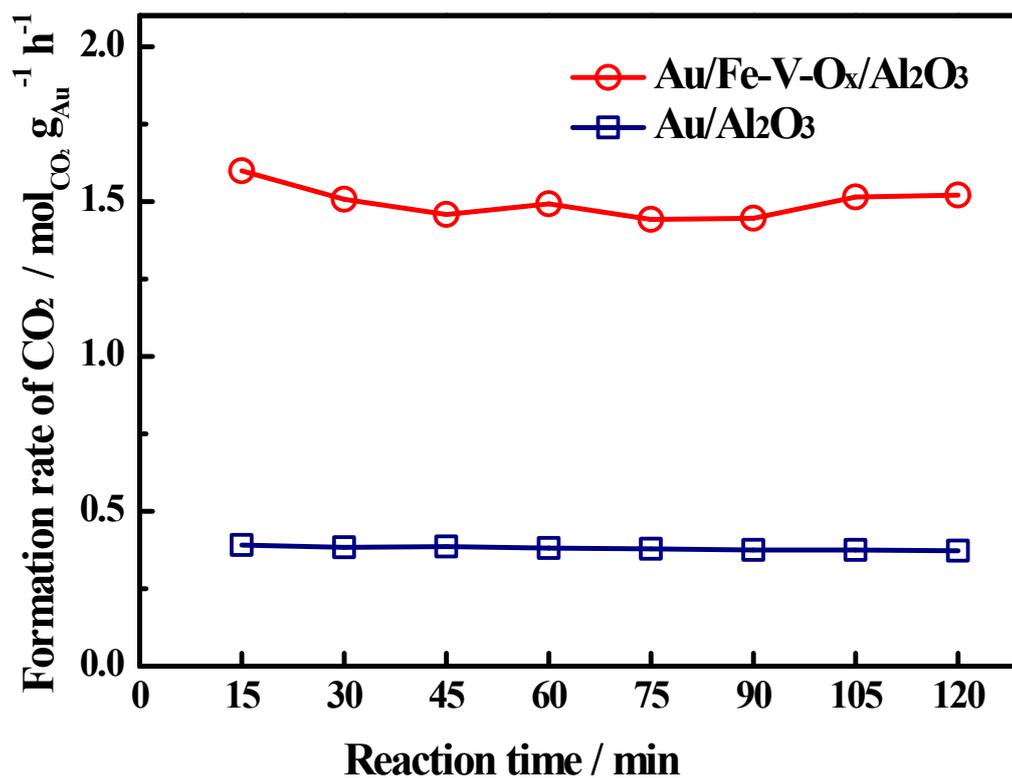**Fig. S7 Raman spectra of Au/Fe-V-O$_x$/Al$_2$O$_3$ catalysts**

Fig. S8 **The specific formation rate of** CO_2 **in the atmosphere of 97%CO in** N_2 **at 220 °C over** Au/Al_2O_3 **and** $Au/Fe-V-O_x/Al_2O_3$ **catalysts**
WHSV: 10, 133 mL g_{cat}^{-1} **h**$^{-1}$