Supporting Information

A highly active Pt-Fe/γ-Al₂O₃ catalyst for preferential oxidation of CO in excess of H₂ with wide operation temperature window

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Table S1 Pt specific reaction rates of the Pt/\gamma-Al\textsubscript{2}O\textsubscript{3} and Pt-Fe/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts.

Reference
Experimental Section

Catalyst preparation

Single Pt and Fe atoms were dispersed onto, via a modified adsorption method\(^1\), the surfaces of Fe\(_2\)O\(_3\) nano-crystallites and \(\gamma\)-Al\(_2\)O\(_3\) (Inframat Advanced Materials and the BET surface area of \(\sim 150 \, \text{m}^2/\text{g}\)) with a nominal loading of 0.5 wt.% for both Pt and Fe. The precursors of Pt and Fe were hexachloroplatinic acid (Sigma-Aldrich) and iron nitrate nonahydrate (Sigma-Aldrich), respectively. The pH values of the Pt- and Fe-containing solutions were finely controlled for each support material to avoid the agglomeration of Pt and Fe. The precursors of Pt and/or Fe were then pumped into water at a speed of \(\sim 0.5 \, \text{ml/min}\) and then the above solution containing Pt (Fe) and \(\gamma\)-Al\(_2\)O\(_3\) (Fe\(_2\)O\(_3\)) was aged for 2 hours at room temperature. After being washed for at least three times to eliminate the residual Cl\(^-\) ions, the resultant powders were dried at 60 °C for 12 h in air. All the samples were then calcined at 300 °C for 4h in air. The actual loading of the Pt/Fe, by ICP-MS (inductively coupled plasma mass spectrometry) technique, was 0.43 wt.% Pt and 0.34 wt.% Fe for the 0.5wt.% Pt-0.5wt.% Fe/\(\gamma\)-Al\(_2\)O\(_3\), 0.32 wt.% Pt for the 0.5wt.% Pt/\(\gamma\)-Al\(_2\)O\(_3\), 0.30 wt.% Fe for the 0.5wt.% Fe/\(\gamma\)-Al\(_2\)O\(_3\), 0.40 wt.% Pt for the 0.5wt.% Pt/Fe\(_2\)O\(_3\), and 0.41 wt.% Pt and 1.36 wt.% Fe for the 0.5wt.% Pt-2.0wt.%Fe/\(\gamma\)-Al\(_2\)O\(_3\), respectively. The corresponding catalysts are denoted as Pt\(_{0.32}/\gamma\)-Al\(_2\)O\(_3\), Fe\(_{0.30}/\gamma\)-Al\(_2\)O\(_3\), Pt\(_{0.43}Fe_0.34/\gamma\)-Al\(_2\)O\(_3\), Pt\(_{0.40}/Fe_2O_3\), and Pt\(_{0.41}Fe_1.36/\gamma\)-Al\(_2\)O\(_3\), respectively.

The Fe\(_2\)O\(_3\) nanocrystallites were synthesized by a precipitation method\(^2\) \(^-\) \(^3\). The ron (III) nitrate nonahydrate (Fe(NO\(_3\))\(_3\)\(\cdot\)9H\(_2\)O, Sigma-Aldrich) was used as a precursor salt, and sodium carbonate (Na\(_2\)CO\(_3\), Sigma-Aldrich) was used as a precipitant. The resultant solid powder precipitates were dried at 60 °C for 12 h and calcined at 350 °C for 4 h in air.

In order to probe the origin of the active centers of our Pt-Fe/\(\gamma\)-Al\(_2\)O\(_3\) catalysts for CO-PROX, Fe atoms with a nominal Fe loading of 0.5 wt.% were deposited on the surfaces of the reduced Pt\(_{0.32}/\gamma\)-Al\(_2\)O\(_3\). The Pt\(_{0.32}/\gamma\)-Al\(_2\)O\(_3\) was pre-reduced before being deposited with Fe atoms by 5 vol.% H\(_2\)/Ar to form Pt nanoclusters. The synthesized catalyst is denoted as Fe\(_x@Pt_{0.32}/\gamma\)-Al\(_2\)O\(_3\).

Evaluation of the catalytic performance

Preferential oxidation of CO experiment was performed in a fixed-bed lab reactor at atmospheric pressure. Typically 30 mg catalyst powders were placed between quartz glass wools.
in a quartz reactor. The reaction mixtures consisted of 1 vol.% CO, 1 vol.% O₂, 50 vol.% H₂ and He balance, and the total gas flow rate was 10.0 ml/min, which corresponded to a weight hourly space velocity (WHSV) of 20,000 ml•g⁻¹•h⁻¹. Before testing the catalytic activity, all the catalysts were pretreated in 5 vol.% H₂/Ar at 300 °C for 2 h. The temperature of the catalyst bed was programmed from 25 °C to 200 °C and the conversion of CO and O₂ was measured by an on-line gas chromatograph (Agilent GC 7890A). The CO and O₂ conversions and selectivity towards O₂ were defined as:

\[ C_{CO} = \frac{[co]_{in} - [co]_{out}}{[co]_{in}} \]  
\[ C_{O_2} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \]

\[ S = \frac{C_{CO}}{\lambda \cdot C_{O_2}} \]

\[ \lambda = 2 \times \frac{[O_2]_{in}}{[co]_{in}} \]

[CO]_{in}/[O₂]_{in}: the concentration of CO/O₂ before reaction; [CO]_{out}/[O₂]_{out}: the concentration of CO/O₂ after reaction.

**Kinetic measurements**

The reaction rates (calculated based on equation (1)) of the synthesized catalysts were measured under a reaction condition of 1 vol.% CO, 1 vol.% O₂, 50 vol.% H₂ and He balance with an weight hourly space velocity of 200,000 ml/g•h at 30 °C and 80 °C.

\[ r = \frac{C_{CO} \cdot X_{CO} \cdot V \cdot P_{atm}}{m_{cat} \cdot R \cdot T} \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{g}^{-1} \cdot \text{cat} \right) \]

Where \( r \) is the reaction rate of catalysts and supports; \( m_{cat} \): mass of catalyst in the reactor bed (g); \( C_{CO} \): concentration of CO in the feed gas; \( V \): total flow rate (m³/s); \( X_{CO} \): conversion rate of CO; \( R \): molar gas constant (8.314 Pa • m³ • mol⁻¹ • K⁻¹); \( T \): temperature (K); \( P_{atm} \): atmospheric pressure (101.3 KPa); \( N_A \): Avogadro constant (6.02 × 10²³ mol⁻¹).
Catalyst Characterization

The loading level of the Pt was measured by a ThermoFinnegan iCAP Q quadrupole ICP-MS with CCT (Collision Cell Technology). Samples were run in KED (Kinetic Energy Discrimination) mode, with in-line aspiration of a multi-element internal standard.

Sub-angstrom resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images were obtained on a JEM-ARM200F TEM/STEM with a guaranteed resolution of 0.08 nm. Before microscopy examination, the catalyst powders were ultrasonically dispersed in ethanol and then a drop of the solution was put onto a copper grid coated with a thin lacey carbon film.

The X-ray photoelectron spectroscopy (XPS) investigation was conducted on a Vacuum Generators 220i-XL using a mono-chromated Al Kα X-ray source (1486.6 eV). The samples were mounted onto the double-sided adhesive tape on the sample holder. The XPS spectra of the selected elements were measured with the constant analyzer pass energy of 20.0 eV. All binding energies (BEs) were referred to the C 1s peak (284.6 eV).

UV-Vis absorption spectroscopy measurements for the Fe$_{0.30}$/γ-Al$_2$O$_3$ and Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ samples reduced by 5.0 vol.% H$_2$/Ar were carried out on a Lambda 18 spectrometer, equipped with a double-beam, double-monochromator, all-reflecting optical system which operates in the ultraviolet (UV) and visible (Vis) spectral ranges. The spectra were recorded in the wavelength range of 200–900 nm. The samples were dispersed into water solvent and ultrasonicated before the measurement.
Figure S1 Pt specific reaction rate of the Pt$_{0.43}$Fe$_{0.34}$/$\gamma$-Al$_2$O$_3$ and Pt-Fe/SiO$_2$ catalysts at 80 °C in presence of CO$_2$ and H$_2$O. Reaction conditions for the Pt$_{0.43}$Fe$_{0.34}$/$\gamma$-Al$_2$O$_3$ catalyst: 1 vol.% CO, 0.5 vol.% O$_2$, 25 vol.% CO$_2$, 20 vol.% H$_2$O, 45 vol.% H$_2$ and He, with a space velocity of 600,000 ml/g•h and pressure of 0.1 MPa. The Pt specific reaction rate of the Pt$_{0.43}$Fe$_{0.34}$/$\gamma$-Al$_2$O$_3$ catalyst was calculated based on the reaction conditions used in the reference$^4$ and the activity contribution of the Fe/SiO$_2$ is assumed to be negligible.

The Pt specific reaction rate of the Pt-Fe/SiO$_2$ catalyst$^1$ for CO-PROX at 80 °C is around 0.33 mol CO•h$^{-1}$•g$_{Pt}$•h$^{-1}$, while the Pt specific reaction rate of the Pt$_{0.43}$Fe$_{0.34}$/$\gamma$-Al$_2$O$_3$ catalyst at 80 °C is 1.78 mol CO•h$^{-1}$•g$_{Pt}$•h$^{-1}$, which is ~5 times higher. These tests proved that the newly developed Pt$_{0.43}$Fe$_{0.34}$/$\gamma$-Al$_2$O$_3$ catalyst possesses excellent CO$_2$ and H$_2$O tolerance.
Figure S2 Particle size distribution of the used Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ (a-d) catalyst after stability test at 30 °C in presence of CO$_2$.

Pt particles of the used Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ (after the stability test as shown in Figure 1d) are uniformly distributed on the surfaces of the γ-Al$_2$O$_3$ support and the average size of the particles is 1.6 ± 0.1 nm.
Figure S3 Particle size distributions of the reduced Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ (a-b) and Pt$_{0.32}$/γ-Al$_2$O$_3$ (c-d) catalysts.
Pt particles of the reduced Pt_{0.43}Fe_{0.34}/γ-Al₂O₃ are uniformly distributed on the surfaces of γ-Al₂O₃ with an average size of 1.8 ± 0.1 nm. Pt particles of reduced Pt_{0.32}γ-Al₂O₃ are uniformly distributed on the surfaces of γ-Al₂O₃ with an average size of 2.3 ± 0.3 nm.
Figure S4 Low-magnification and high-magnification aberration-corrected HAADF/STEM images of the fresh Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ catalyst. M$_1$ stands for single Pt atoms.

As clearly shown in Figure S4 (a-b), low-magnification HAADF-STEM images confirm the absence of any Pt or Fe particles or clusters in the fresh Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ catalyst. The high-magnification HAADF-STEM images confirm that both the Pt and/or Fe atoms are atomically dispersed on the surfaces of the γ-Al$_2$O$_3$ support. By examining numerous low/high magnification HAADF-STEM images (Figure S4 (a-f)) obtained from different regions, we unambiguously concluded that the fresh Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ catalyst contains only isolated Pt and Fe atoms.
Figure S5 XPS spectra of the Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ catalysts: fresh (a) and reduced (b).

The catalyst reduction condition: 5 vol.% H$_2$/Ar at 300 °C for 2h. The Fe 2p$_{3/2}$ peak located at 708.9 eV can be attributed to the Fe$^{2+}$ species$^{5,6}$. Fe species of the reduced Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ (reduced at 300 °C for 2h in 5 vol.% H$_2$/Ar) catalysts exhibited the same oxidation state as that of the fresh Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ catalyst, which indicates that the Fe species were still atomically dispersed during H$_2$ reduction since the oxidation state of Fe species should be significantly changed once the single FeO species sinter to form overlayer or cluster structures$^{4,7}$.

Three oxidation states of Fe species, Fe$^0$, Fe$^{2+}$ and Fe$^{3+}$, have been identified for catalytic reactions of CO-PROX. However, previous report has proved that the Fe$^{3+}$ species can not efficiently activate O$_2$ during CO-PROX$^3$. DFT calculations have shown that O$_2$ adsorption on metallic Fe is too strong to be reactive for CO-PROX$^4$. From these reported results we can conclude that the Fe$^0$ and Fe$^{3+}$ species may not be the active species for O$_2$ activation during CO-PROX. On the other hand, it has been proposed, via $^{57}$Fe Mossbauer spectroscopy$^9$ and XPS$^{10}$ studies, that the Fe$^{2+}$ species are the active centers for O$_2$ activation during CO-PROX. From these reported results and our experimental data we propose that the single Fe$^{2+}$ species, which are in intimate contact with the Pt clusters, in our Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ catalyst play a major role for the CO-PROX reaction.
**Figure S6** UV-Visible spectra of the reduced Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ and Pt$_{0.32}$/γ-Al$_2$O$_3$ catalysts. The Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ and Pt$_{0.32}$/γ-Al$_2$O$_3$ samples were reduced by 5.0% H$_2$/Ar at 300 °C for 2h.

The metal-ligand charge transfer of metal ions with d$^n$ configuration are associated with characteristic spectroscopic features, which can be used as a fingerprint for the recognition of the oxidation and coordination states of transition metal ions.$^{11-14}$ Hence, UV-Visible spectroscopy was used to investigate the nature of the Fe species in the reduced Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ sample.$^{}$

As shown in Figure S6, there is no absorbance band for the Pt$_{0.32}$/γ-Al$_2$O$_3$ sample but the reduced Pt$_{0.43}$Fe$_{0.34}$/γ-Al$_2$O$_3$ sample shows a weak absorption band centered at 270 nm, which can be assigned to the charge transfer from Fe to O. The isolated Fe$^{3+}$ species, represented by an absorption band at 250 nm$^{13, 14}$ is absent. Hence, the weak absorption band centered at 270 nm can be assigned to the isolated Fe$^{2+}$ species. The UV-Vis data further confirms that the Fe species were still atomically dispersed on the surfaces of γ-Al$_2$O$_3$ during H$_2$ reduction.
Figure S7 Low-magnification and high-magnification aberration-corrected HAADF/STEM images of the Fe$_{0.30}$/$\gamma$-Al$_2$O$_3$ catalyst after H$_2$ reduction at 300 °C for 2h in 5 vol.% H$_2$/Ar.

As clearly shown in Figure S7 (a), low-magnification HAADF-STEM images confirm the absence of any Fe particles or clusters in the Fe$_{0.30}$/$\gamma$-Al$_2$O$_3$ after H$_2$ reduction at 300 °C for 2h. The high-magnification HAADF-STEM images confirm that Fe atoms are atomically dispersed on the surfaces of the $\gamma$-Al$_2$O$_3$ support. By examining the low/high magnification HAADF-STEM images obtained from different regions, we unambiguously conclude that the Fe$_{0.30}$/$\gamma$-Al$_2$O$_3$ reduced by H$_2$ contains only isolated Fe atoms without any Fe particles or clusters.
Figure S8 High-temperature stability test of the Pt$_{0.43}$Fe$_{0.34}$/$\gamma$-Al$_2$O$_3$ catalyst from 120 °C to 200 °C: (a) CO conversion and (b) O$_2$ conversion. Reaction condition: 1 vol.% CO, 1 vol.% O$_2$, 50 vol.% H$_2$ and He balance, GHSV = 300,000 ml•g$^{-1}$•h$^{-1}$.

As shown in Figure S8 (a-b), the Pt$_{0.43}$Fe$_{0.34}$/$\gamma$-Al$_2$O$_3$ catalyst did not show any hysteresis behavior during the heating and cooling cycle, reflecting the fact that the active centers are stable during the catalytic reaction. Such behavior is totally different from the previously reported Pt-Fe alloy systems of which phase segregation to metallic Pt and FeO$^{10}$ and/or re-oxidation of the active ferrous (Fe$^{2+}$) species to inactive ferric (Fe$^{3+}$) species$^8$ can occur.
Figure S9 Schematic diagram illustrates the proposed structure of the Fe,/Pt,0.32/γ-Al₂O₃ catalyst.

We assume that the Pt clusters have a shape of semi-spheres on the surfaces of γ-Al₂O₃, and the diameter of these semi-spheres is 2.3 nm (Figure S3). Then the total surface area of each Pt cluster is 8.3 nm², the volume of each Pt cluster is 3.2 nm³ and the total weight of each Pt cluster is 6.8 x 10⁻²⁰ g.

For 1g Fe,/Pt,0.32/γ-Al₂O₃ catalysts, the total weight of Pt is 0.0032g, resulting in the total number of Pt clusters on the surfaces of the γ-Al₂O₃ support of ~4.6 x 10¹⁶. And the total surface area of all Pt clusters is ~0.4 m². Then the ratio of the total surface area of all the Pt clusters to the total surface area of the support (γ-Al₂O₃) is ~2.6 x 10⁻³. The BET surface area of γ-Al₂O₃ is 150 m²/g.

For 1g Fe,/Pt,0.32/γ-Al₂O₃ catalysts, the total theoretical weight of Fe is 0.005g, resulting in the total number of Fe atoms of ~5.4 x 10¹⁹. Considering the uniform dispersion of single Fe atoms on the surfaces of the γ-Al₂O₃ (Figure S7), we can reasonably assume that all of the single Fe atoms are uniformly dispersed onto the surfaces of the support (γ-Al₂O₃) and the Pt clusters. Then the total Fe atoms on the surfaces of all Pt clusters is ~1.4 x 10¹⁷, resulting in, on average, 3 Fe atoms per Pt cluster.
When the surfaces of the Pt particles were covered by single FeOₓ species, even with extremely low loading levels, the catalytic activity of the Pt₀.₃₂/γ-Al₂O₃ catalyst can be greatly enhanced compared with that of the Pt₀.₃₂/γ-Al₂O₃ catalyst, suggesting that the presence of the single FeOₓ species plays a crucial role in determining the catalytic performance of the Pt-Fe/γ-Al₂O₃ catalysts for CO-PROX. When the surfaces of the Pt particles were covered by excessive Fe atoms, the CO conversion of the Pt₀.₄₁Fe₁.₃₆/γ-Al₂O₃ catalyst was dramatically decreased compared with that of Pt₀.₄₃Fe₀.₃₄/γ-Al₂O₃ catalyst, suggesting that only when appropriate amount of Pt surfaces and the FeOₓ species are simultaneously accessible by the reactants the catalytic reactions with desired activity and selectivity can be obtained since both CO adsorption and O₂ activation are simultaneously optimized.

Figure S10 CO conversion of the Pt₀.₄₁Fe₁.₃₆/γ-Al₂O₃ (■), Pt₀.₄₃Fe₀.₃₄/γ-Al₂O₃ (●), Pt₀.₄₃Fe₀.₇/γ-Al₂O₃ (Φ) and Pt₀.₃₂/γ-Al₂O₃ (◊) catalysts for CO-PROX in the feed gas of 1 vol.% CO, 1 vol.% O₂, 50 vol.% H₂ and He with a weight hourly space velocity of 20,000 ml/g•h.
Table S1 Pt specific reaction rates of the Pt/γ-Al₂O₃ and Pt-Fe/γ-Al₂O₃ catalysts

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<th>Temperature /°C</th>
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a: FeₓPt₀.32/γ-Al₂O₃ with nominal Fe loading of 0.5 wt.%; Pt species are pre-reduced before depositing Fe atoms by 5 vol.% H₂/Ar to form nanoparticles.

Reference